Aust. J. Phys., 1985, **38**, 677–85

Low Energy Electron Collision Cross Sections for Methane

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Abstract

Measurements of the drift velocity v_{dr} and the ratio of the lateral diffusion coefficient to mobility $D_\perp/\mu$ have been made in pure methane at 293 K. Measurements of v_{dr} and $D_\perp/\mu$ were made for values of E/N (the electric field strength divided by the number density) ranging from 0·03 to 14 Td and 0·02 to 12 Td respectively (1 Td $\equiv 10^{-21}$ V m^2). The estimated accuracy of the results is $\pm 1\%$ for v_{dr} and $\pm 2\%$ for $D_\perp/\mu$. The data have been analysed by means of a multiterm solution of the Boltzmann equation to provide a set of low energy electron collision cross sections consistent with the transport data.

1. Introduction

Because it is the simplest of all organic molecules there has been continuous interest in low energy electron scattering from methane over the past half century. The broad features of the elastic cross section at low energies are known (see e.g. Massey *et al.* 1969; Duncan and Walker 1972); there is a Ramsauer–Townsend minimum at about 0·3 eV rising to a broad maximum at about 7 eV. There is, however, considerable doubt about the detailed shape of both this cross section and the inelastic cross sections.

A knowledge of very low energy electron scattering cross sections for methane is important in attempting to optimize the characteristics of diffuse discharge switches (Christophorou *et al.* 1982; Schoenbach *et al.* 1982). Kline (1982) has proposed this type of device to transfer energy from inductive storage loops to a load. The optimization of these devices involves the choice of a gas mixture with high conductivity when the switch is 'closed'. Methane, with its high drift velocity at low values of E/N, is a candidate gas for such devices. In addition, many proportional and drift counters contain methane and there have been several attempts to explain some aspects of the behaviour of these devices in terms of the electron scattering cross sections for the filling gas (Palladino and Sadoulet 1975; Schultz and Gresser 1978).

Electron swarm experiments have provided much of the presently available information about electron–molecule interactions for electron energies below about 1 eV, and they remain the sole source of information at thermal energies. However,

0004-9506/85/050677$02.00

swarm experiments by themselves are often unable to provide a unique set of elastic and inelastic cross sections derived from the measured transport data (Crompton 1983). Therefore, a successful determination of both types of cross sections often requires a combination of swarm measurements and single collision measurements, combined with theoretical calculations of cross sections.

To analyse swarm data it is necessary to relate the scattering cross sections to the transport coefficients through a solution of the Boltzmann equation. Most previous derivations of cross sections from swarm data have used the two-term approximation to solve this equation, but it is now widely recognized that in methane this approximation fails for values of E/N larger than about 0·4 Td (Lin *et al.* 1979; Braglia 1981; Pitchford *et al.* 1981).

The present paper presents measurements of both the drift velocity v_{dr} and the ratio of the lateral diffusion coefficient to mobility $D_\perp/\mu$ in pure methane over a wide range of E/N. The data are analysed using a multiterm solution of the Boltzmann equation to derive elastic and inelastic cross sections which are consistent with the swarm data.

Section 2 discusses the experimental procedures, while the results of the measurements are presented in Section 3. In Section 4 we discuss the solution of the Boltzmann equation and the method of fitting the transport data to provide cross sections. We also present the derived cross sections and compare them with previous results.

2. Experimental Procedures

Both the drift velocity apparatus and the lateral diffusion apparatus used for the present measurements have been described previously (Crompton *et al.* 1968; Milloy and Crompton 1977). The drift velocity measurements were made with the semi-automatic control and data-handling system described previously by Haddad (1983).

The methane used was Matheson Research Grade (99·99% pure) which was further purified by passing the gas over a freshly evaporated titanium film. The titanium getter absorbs impurities but does not react with methane (Winters 1975).

As pointed out by Crompton *et al.* (1968), a trace amount of molecular oxygen (of the order of a few parts in 10^{10}) can cause significant changes to the current ratios measured in the diffusion apparatus. With this degree of contamination Crompton *et al.* (1968) measured an anomalous dependence of $D_\perp/\mu$ on current in their experiments in hydrogen which was accounted for by extrapolating the measurements to zero current. Where necessary, the measurements of $D_\perp/\mu$ reported in the present paper were corrected by the same technique, i.e. by measuring the current ratios with currents of 1 and 2×10^{-12} A and extrapolating to zero current. With methane taken directly from the cylinder we observed differences of up to 5% between the extrapolated value of $D_\perp/\mu$ and the value recorded at the lowest current. After purification the maximum difference was 0·7% and this difference decreased rapidly with increasing E/N. The current dependence was measured immediately after the diffusion apparatus was filled with gas and just prior to removing the gas at the end of a series of measurements. No difference could be detected, confirming that there was no contamination of the sample during the time taken to make the measurements.

In the drift velocity experiment, impurities can cause a sloping background in the plot of current against frequency (Elford 1971). No such background was observed with the purified methane and the measured drift velocities were repeatable to within ±0·1% from day to day.

Table 1. Drift velocities and lateral diffusion coefficient to mobility ratios for methane at 293 K

E/N (Td)	v_{dr} (10^3 m s^{-1})	$D_\perp/\mu$ (mV)	E/N (Td)	v_{dr} (10^3 m s^{-1})	$D_\perp/\mu$ (mV)
0·02	—	27·3	0·6	28·6	49·5
0·025	—	27·6	0·7	34·6	54·0
0·03	0·94	28·0	0·8	40·8	58·6
0·035	1·11	28·3	1·0	52·8	68·2
0·04	1·28	28·6	1·2	63·8	78·3
0·05	1·62	29·0	1·4	73·4	89·0
0·06	1·97	29·4	1·7	84·9	106
0·07	2·33	29·8	2·0	93·2	124
0·08	2·68	30·1	2·5	102	158
0·1	3·41	30·8	3·0	105	195
0·12	4·16	31·4	3·5	106	235
0·14	4·94	32·1	4·0	105	279
0·17	6·14	33·1	5·0	101	375
0·2	7·40	34·1	6·0	94·9	480
0·25	9·62	35·8	7·0	89·4	591
0·3	12·0	37·5	8·0	84·5	706
0·35	14·5	39·3	10·0	76·1	941
0·4	17·1	41·2	12·0	70·1	1180
0·5	22·7	45·2	14·0	65·7	—

3. Experimental Results

The experimental results are presented in Table 1. Measurements of the drift velocity were made at seven pressures within the range 2·07–40·3 kPa with measurements at any given value of E/N being made at a minimum of three different pressures and in some cases up to six pressures within the range specified above. The maximum deviation in the measured values of v_{dr} for various pressures at a given value of E/N is 0·3%; the results presented in Table 1 are mean values.

Similarly, measurements of $D_\perp/\mu$ were made at ten pressures within the range 1·34–68·2 kPa, again with a minimum of three different pressures at each value of E/N. The maximum deviation in measured values of $D_\perp/\mu$ at a given value of E/N is 0·5% and, as for the drift velocities, the results shown in Table 1 are mean values.

Error limits were determined by adding the systematic and random errors. Since the total systematic error was obtained by adding the contributions arithmetically, the final assigned error may be regarded as the estimated maximum possible error. A detailed discussion of errors in these types of measurements has been given previously (Elford 1971). By taking all sources of error into account, the values of v_{dr} were estimated to be accurate to within ±1% and the values of $D_\perp/\mu$ to within ±2%.

The present results for v_{dr} are compared in Fig. 1 with previous measurements by Pollock (1968). There is general agreement with the results of Pollock and also of Wagner *et al.* (1967). Previous measurements have stated accuracies of 1–3% (Pollock 1968), 4% (El-Hakeem and Mathieson 1979) or are not specified. A similar comparison of our results for $D_\perp/\mu$ with the previous measurements of Duncan and Walker (1972) is made in Fig. 2. At low values of E/N our results are generally

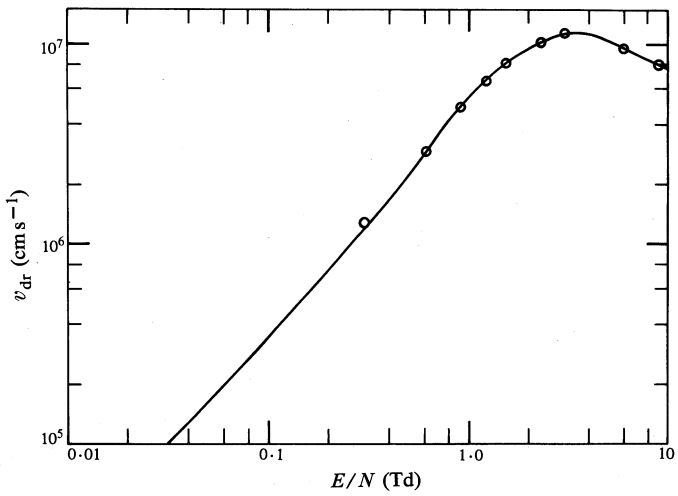

Fig. 1. Drift velocities in methane. Previous results by Pollock (1968) are shown as circles.

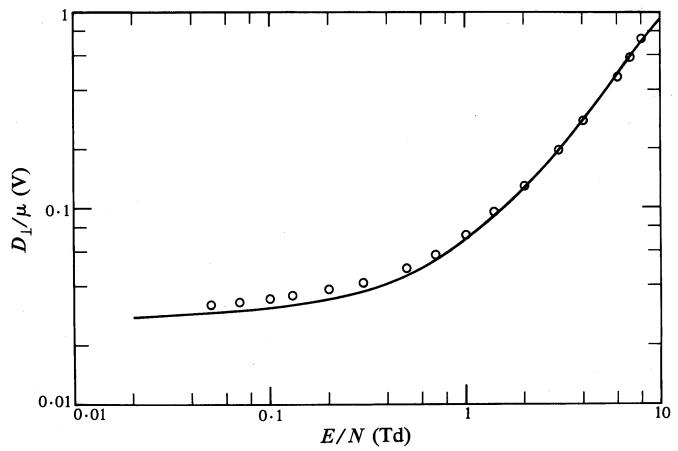

Fig. 2. Lateral diffusion coefficient to mobility ratios in methane. Previous results by Duncan and Walker (1972) are shown as circles.

lower than the previous work for reasons which are not understood. The accuracy of the previous measurements is $\pm 5\%$.

4. Analysis and Results

A multiterm solution of the Boltzmann equation to calculate transport coefficients requires both the total cross sections and the angular distributions for the various processes. In our analysis we have used isotropic angular distributions for all processes, because adequate information for electron scattering in methane is lacking. The information available in the literature is limited to energies which are higher

than those required for the present analysis and is also limited in terms of the angular range of the data (Rohr 1980; Tanaka *et al.* 1982).

Two different numerical methods of solving the Boltzmann equation were used to derive the cross sections. The first method is a conventional two-term solution developed by Gibson (1970) and the second is a multiterm solution developed by Lin *et al.* (1979) which uses the moment method (see also Haddad *et al.* 1981). The differences between the two-term and multiterm calculations are shown in Fig. 3. Differences in both v_{dr} and $D_\perp/\mu$ are a maximum at around $E/N = 4$ Td which corresponds to a mean swarm energy of about 0·3 eV. This is approximately the energy of both the minimum in the elastic scattering cross section and the maximum of the sum of the inelastic cross sections. This confirms the conclusions of previous work (see e.g. Reid 1979) that the two-term approximation can be expected to be inadequate when the ratio of inelastic to elastic cross sections is large.

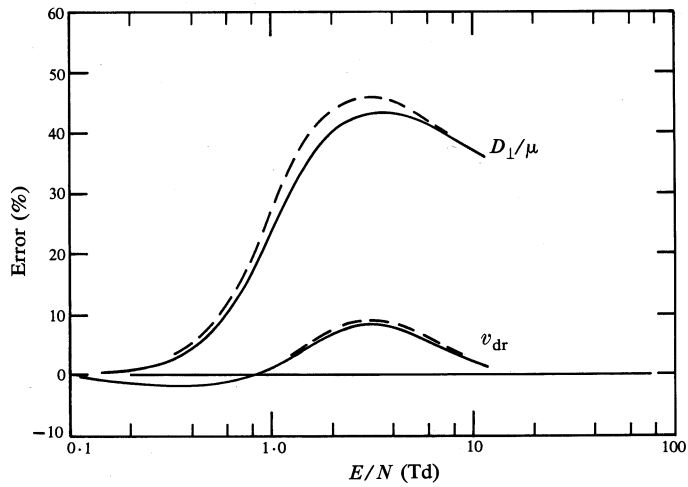

Fig. 3. Differences in the transport coefficients, calculated using two-term and multiterm solutions of the Boltzmann equation for methane. The solid curves are calculated with isotropic scattering and the dashed curves with anisotropic scattering (see Section 4).

As shown in Fig. 3 the errors incurred in using a two-term solution of the Boltzmann equation to calculate transport coefficients for methane are as large as 50%. The cross sections derived by fitting transport data with such a solution would therefore be significantly in error. This, rather than the difference in the transport data that were analysed, accounts for the dramatic differences between our derived cross sections near the minimum and those obtained by Duncan and Walker (1972) who used a two-term code for their analysis.

As shown in Figs 1 and 2 the differences in the transport coefficients used by Duncan and Walker and in our work are significant—of the order of 15%. The largest difference occurs for the $D_\perp/\mu$ data at very low values of E/N. At low energies the Duncan and Walker momentum transfer cross section is approximately proportional to ϵ^{-2}, and they commented that this dependence cannot be accounted for by simple potential scattering (an electron–dipole interaction gives an ϵ^{-1} variation). Our

cross section is approximately proportional to ϵ^{-1} at low energies. The reason for this difference between the two results is a reflection of the differences between the transport data. The fact that Duncan and Walker used a two-term solution of the Boltzmann equation is not relevant since in this range of very low energies (corresponding to low values of E/N) the difference between transport parameters, calculated with either two-term or multiterm solutions, is negligible.

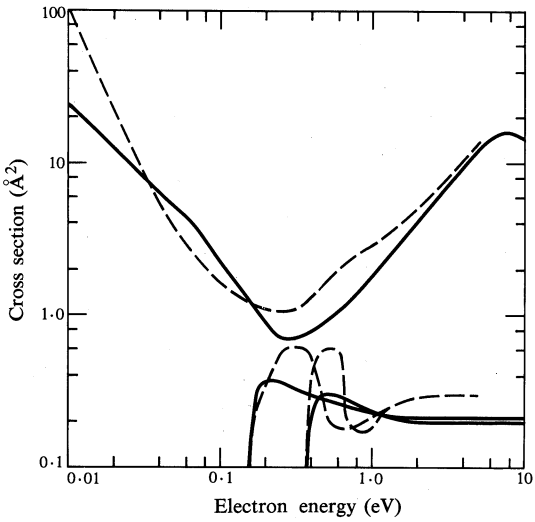

Fig. 4. Derived cross sections for methane (solid curves) compared with the previous results of Duncan and Walker (1972) (dashed curves).

Fig. 4 shows that our derived momentum transfer cross section is about 30% lower than that of Duncan and Walker in the region of the minimum (around 0·3 eV). This difference is a reflection of the large error in a two-term solution of the Boltzmann equation, as illustrated in Fig. 3.

The initial set of cross sections for our analysis were taken from the work of Duncan and Walker and, following their work, we have completely neglected the effect of rotational excitation. Rotational excitation can only occur via octopole or higher moments so that the rate of energy loss is expected to be small. Unfortunately, neither theoretical (Jain and Thompson 1982, 1983) nor experimental (Tanaka *et al.* 1982, 1983) information on rotational excitation is available at sufficiently low energies.

Although it is known that there is considerable structure in the energy dependence of the momentum transfer cross section in methane, there is little information from single collision experiments on the shape of the inelastic cross sections and, until very recently (Ferch *et al.* 1985), little data on the shape of the momentum transfer cross section. This presents a problem in uniquely determining each of the cross sections by analysing swarm data. If, for example, the momentum transfer cross sections were known to be a monotonic function of energy (as it is in hydrogen), or if there were no inelastic channels open at energies where there is a strong energy dependence in the momentum transfer cross section (as in the case of argon), the situation would

be much simpler. In the case of methane, adjustments to the inelastic cross sections can be compensated for by corresponding adjustments to the momentum transfer cross section in order to maintain the same quality of fit between measured and calculated transport data. Although we have not explored the full extent of this interchangeability it appears that a 50% change to the inelastic cross sections over a particular energy range can be compensated for by a 30% variation in the momentum transfer cross section. Such large variations in the momentum transfer cross section are restricted to energies near the minimum (say 0·15–0·6 eV).

For a given set of inelastic cross sections, the shape and magnitude of the momentum transfer cross section are constrained. Nevertheless, it is still possible to choose between a 'smooth' *total* momentum transfer cross section in the region of the minimum which results in a 'non-smooth' *elastic* momentum transfer cross section, or vice versa. Previous work (Barbarito *et al.* 1979; Sohn *et al.* 1983) suggests that the elastic momentum transfer cross section is fairly smooth in the region near the minimum and we have chosen to follow this suggestion in our analysis. Very recent results by Ferch *et al.* (1985) confirm our choice. The maximum difference between the momentum transfer cross sections described as 'smooth' or 'non-smooth' above is of the order of 15%, i.e. with a given set of inelastic cross sections there is a lack of uniqueness in this analysis which amounts to an uncertainty of about 15% in the value of the momentum transfer cross section near the minimum.

In the early stages of our analysis we used the inelastic cross sections of Duncan and Walker. However, there have been two recent measurements of low energy inelastic scattering cross sections in methane (Rohr 1980; Sohn *et al.* 1983). Both papers presented differential cross sections over a limited range of angles, rather than total cross sections. Angular integration of the results from either of these experiments will suffer from extrapolation uncertainties which are difficult to assess. Finally, to emphasize the problem of determining cross sections for individual processes we note that Duncan and Walker demonstrated that the swarm data can be fitted adequately by using only one inelastic cross section rather than the two suggested by the single collision experiments.

There is clearly a good deal of arbitrariness in the choice of the inelastic cross sections for the swarm analysis. Accordingly we used two cross sections having no more than only the general features of those presented by Sohn *et al.* (1983). Although Fig. 4 shows inelastic cross sections extending to an energy of 10 eV, the calculated transport coefficients up to E/N values of 12 Td (the upper limit of our measurements) are insensitive to the shape of the cross sections beyond about 5 eV. The work of Tanaka *et al.* (1983) showed a broad maximum in the vibrational cross sections at around 7 eV which is not inconsistent with the present results. It should be emphasized that the shape of the vibrational cross sections is arbitrary and can only be fixed by more definitive results from either single collision experiments or theory. Having chosen this set of inelastic cross sections and elected to use a 'smooth' elastic momentum transfer cross section, we can determine the magnitude and shape of the total momentum transfer cross section by fitting the measured transport coefficients to the values calculated with the multiterm solution of the Boltzmann equation. The derived cross section is shown in Fig. 4 together with our chosen inelastic cross sections.

Multiterm calculations with anisotropic angular scattering distributions may show significant differences from similar calculations made with isotropic distributions (see

e.g. Haddad *et al.* 1981). Data on low energy angular scattering distributions in methane are not readily available. The recent work of Sohn *et al.* (1983) provided some information over a limited range of both energies and angles for elastic and inelastic scattering. In attempting to assess the effect of anisotropic angular scattering on our analysis we have used data for elastic scattering at 1 eV and for inelastic scattering in the $\nu_{2,4}$ channels at 0·3 eV taken from this work. We have arbitrarily extrapolated the published information to 0° and 180° and used the appropriate angular dependences described above at all energies. The results of multiterm calculations using cross sections with these angular dependences are shown in Fig. 3. The largest differences between the calculations with isotropic and anisotropic distributions occur in the values of $D_\perp/\mu$ and are limited to about 4%. Errors of this magnitude may certainly be significant, but given the uncertainty in the angular distributions and the lack of uniqueness in the derived cross sections discussed previously, we have not yet made any attempt to derive cross sections with other than isotropic angular scattering distributions.

5. Conclusions

This paper presents accurate measurements of v_{dr} and $D_\perp/\mu$ in pure methane at 293 K over a wide range of E/N. The data are analysed using a multiterm solution of the Boltzmann equation to derive a set of cross sections consistent with the transport data.

The accuracy of both the derived momentum transfer and inelastic cross sections is difficult to assess. It is, however, demonstrated that unless the swarm data are analysed by using a multiterm solution of the Boltzmann equation, the derived set of cross sections will be substantially in error. With the advent of more complete data from single collision experiments the uniqueness problem can be solved and these data can be used to provide a set of accurate cross sections.

Acknowledgments

This work was completed with the aid of a joint CSIRO–ANU research grant. The author would like to thank Dr R. E. Robson and Dr K. Ness for the use of the multiterm code and Dr R. W. Crompton and Dr L. E. Cram for many helpful discussions.

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Manuscript received 28 March, accepted 7 August 1985