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Electron Transport Coefficients in Carbon Monoxide and Deuterium

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Abstract

The drift velocity and the ratio of transverse diffusion coefficient to mobility have been measured for electrons in gaseous carbon monoxide and deuterium at 293 K. The measurements were made under conditions where vibrational excitation is the major energy loss in order to resolve some discrepancies that exist between published vibrational excitation cross sections for these gases. The results are in good agreement with the majority of the existing data where available, but the error bounds are reduced significantly in some cases.

1. Introduction

Transport data for low energy electrons have been widely used for the determination or normalisation of elastic and inelastic scattering cross sections, particularly for inelastic processes with low threshold energies (see e.g. Crompton 1983 and references therein). For this application data of high accuracy are required in order to obtain the derived cross sections with adequate accuracy and uniqueness (Huxley and Crompton 1974; Morrison *et al.* 1987).

Hake and Phelps (1967) were the first to analyse electron transport data for CO to determine a set of elastic and inelastic cross sections compatible with the data for CO then available. The most interesting feature of their results was the demonstration of the importance of non-resonant vibrational excitation at energies less than 1 eV before the onset of the $^2\Pi$ shape resonance with its maximum at about 2 eV. Lack of reliable transport data limited their determination of the cross sections to energies less than 1 eV. With the availability of new drift velocity (v_{dr}) data (Milloy 1977), Land (1978) was able to extend the analysis to include the resonance, basing his work on Milloy's data and also data for the transverse diffusion coefficient to mobility ratio D_T/μ of Skinker and White (1923) and Lakshminarasimha *et al.* (1974). A significant result of this work was his conclusion that, in order to obtain reasonable agreement between calculated and measured transport coefficients, it was necessary to apply a scaling factor of 1·9 to the set of vibrational excitational cross sections determined by Ehrhardt *et al.* (1968) from their beam experiment.

Haddad and Milloy made a further study of the resonance region in their 1983 paper. By basing their analysis on Milloy's 1977 v_{dr} data for CO–He

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and CO–Ar mixtures, they were able to avoid three problems inherent in Land's work: its reliance on the very early D_T/μ data of Skinker and White; the use of a Boltzmann transport code based on first order approximations (as universally used at that time); and the lack of separation between the effects of elastic and inelastic processes. Haddad and Milloy found that a scaling factor of 1·3 rather than 1·9 gave the best agreement between their calculated and experimental v_{dr} data. The disagreement between the scaling factors was attributed primarily to the inadequacy of the approximations in the transport code used in the earlier work. Land had attempted to compensate for errors introduced by these approximations by applying corrections that were based on the work of Kontoleon *et al.* (1973). However, Haddad and Milloy showed that corrections became necessary at values of the reduced electric field strength E/N (N is the gas number density) where the transport coefficients were strongly influenced by scattering in the resonance region but where Land had assumed the corrections to be still negligible. Nevertheless, although they were able to make a convincing case for a much lower value for the normalising factor, some discrepancies remained between the transport coefficients calculated with their cross sections and available transport data (see Section 4).

Elastic and inelastic cross sections for deuterium were first derived from an analysis of transport coefficients by Engelhardt and Phelps (1963) and later by Gibson (1970). In the latest work by Buckman and Phelps (1985) a detailed analysis was made of both transport and excitation rate coefficient data in an attempt to find a set of cross sections compatible with all available data. These authors stressed the need for more accurate transport data in the intermediate range of E/N where vibrational excitation is the dominant energy loss process.

Thus for both CO and D_2, recent work has pointed to a lack of reliable data for either one or both transport coefficients in certain ranges of E/N. In this paper we present data for the drift velocity and D_T/μ for these gases at 293 K in E/N ranges for which data have not been previously reported from these laboratories or, to our knowledge, were not otherwise available when this work was carried out.

2. Previous Measurements

(a) Carbon Monoxide

Only a limited number of data sets for D_T/μ and v_{dr} for electrons in CO exist in the literature. Values of D_T/μ were measured by Warren and Parker (1962) in the low E/N range at 77 K. The room-temperature results of Skinker and White (1923) and Roznerski and Mechlinska-Drewko (1979) extend over the entire range of E/N covered by us in the present study, while the lower end of the E/N range investigated by Lakshminarasimha *et al.* (1974) overlaps the upper range of our measurements. Nelson and Davis (1969) measured the diffusion coefficient for thermal electrons, while Wagner *et al.* (1967) measured values of the longitudinal diffusion coefficient D_L.

Drift velocities for electrons in CO were measured by Pack *et al.* (1962) (at three different temperatures including room temperature), by Wagner *et*

al. (1967), by Saelee (1976; see also Saelee and Lucas 1977) at high values of E/N, and by Roznerski and Leja (1984) over a very wide range of values of E/N. Milloy (1977) measured drift velocities in pure CO between 10 and 100 Td (1 Td $\equiv 10^{-17}$ V cm^2) and also made measurements in Ar–CO and He–CO mixtures. An interesting feature of his mixture results is the occurrence of negative differential conductivity (Petrović *et al.* 1984; Robson 1984), although the effect was not as pronounced as predicted by Long *et al.* (1976). Recently, after the preliminary reports of our data (Petrović and Crompton 1984), Nakamura (1987) published values of drift velocities for CO (and N_2) in the region between 0·3 and 300 Td, together with data for D_L/μ.

(b) Deuterium

The sets of data for D_T and ν_{dr} in D_2 are more numerous but nevertheless inadequate in the range of swarm energies where vibrational excitation is the dominant inelastic process. Measurements of drift velocity include those of Pack *et al.* (1962), McIntosh (1966), Crompton *et al.* (1968), Robertson (1971), and Crompton and Robertson (1971). Measurements of D_T/μ have been made by Hall (1955), Warren and Parker (1962), McIntosh (1966), and Crompton *et al.* (1968). Creaser (1967) published data for the magnetic deflection coefficient. Recently, Buckman and Phelps (1985) published an account of their detailed study of excitation coefficients in mixtures of D_2 with various tracer gases.

3. Experimental Details

(a) Measurements of Drift Velocity

Drift velocities were measured by using the Bradbury–Nielsen technique as described by Huxley and Crompton (1974). The raw data for the drift velocities, given simply by dividing the drift distance h by the transit time t_m, were corrected for the effects of diffusion on the travelling pulses in flight and at the shutters by applying the formula

$$\nu_{dr} = (h/t_m)[1 - C(D_T/\mu)/V], \tag{1}$$

where V is the potential difference between the planes of the shutters. The constant C was determined empirically from the results recorded at several pressures (Elford 1972). For each gas a single value of C was found to fit the data adequately at all values of E/N where data at more than one pressure could be recorded. The same value was therefore adopted to correct the raw data at the extremes of the range of E/N where limitations to the experimental parameters restricted the measurements to a single pressure.

(b) Measurements of the Diffusion Coefficient to Mobility Ratio

Measurements of D_T/μ were made by the standard Townsend–Huxley method (Huxley and Crompton 1974) using two apparatuses that have been used and described previously. One of the two, a fixed-length (10 cm) apparatus with a single choice of anode configuration (Crompton *et al.* 1965), was designed to meet stringent requirements of mechanical stability and dimensional tolerance, and as such is intrinsically capable of producing the more accurate results

where it can be used. However, for a given gas its fixed configuration limits the range of E/N and N for which it can be used because of such factors as the maximum voltage that can be applied to the apparatus before the onset of electrical breakdown, and the field strength and pressure that lead to an appropriate distribution of current between the two segments of the anode. The second apparatus, whose cathode–anode separation and anode configuration can be varied (Crompton and Jory 1962), enables the range of experimental parameters to be expanded considerably, but at the cost of some loss of accuracy.

The distribution of electron number density n between the cathode and anode of such an apparatus can be adequately represented by a solution of the time-independent equation

$$D_T\left(\frac{\partial^2 n}{\partial x^2}+\frac{\partial^2 n}{\partial y^2}\right)+D_L\frac{\partial^2 n}{\partial z^2}=v_{dr}\frac{\partial n}{\partial z}, \tag{2}$$

with the boundary condition $n=0$ at the cathode and anode. It can be shown that for most of the experimental conditions used in these experiments (determined by apparatus geometry and stream divergence), the ratio R of the current received by the central circular area of the anode of radius b to the total current is given with sufficient accuracy by (Lowke 1971; Huxley 1972; see also Huxley and Crompton 1974)

$$R=1-\left\{1+\left(\tfrac{1}{2}-\frac{D_L}{D_T}\right)\left(\frac{b}{d}\right)^2\right\}\frac{h}{d}\exp\{-\lambda(d-h)\}, \tag{3}$$

where h is the cathode–anode separation, $d^2=b^2+h^2$, and $\lambda=v_{dr}/2D_T$. (Note that the dimensions of the two apparatuses and the experimental conditions were chosen so that the electron number density fell to a negligible value well inside the inner diameter of the cylindrical guard structure, obviating the necessity of specifying a radial boundary condition.)

When $D_L/D_T\approx 0\cdot 5$, corresponding to the case of a constant or slowly varying momentum transfer cross section, the formula (3) for the current ratio may be replaced by

$$R=1-(h/d)\exp\{-\lambda(d-h)\}, \tag{4}$$

the so-called 'Huxley formula'. This formula also holds sufficiently accurately when D_L/D_T differs significantly from $0\cdot 5$ provided h is sufficiently large and b sufficiently small. For example, when $h=10$ and $b=0\cdot 5$ cm, corresponding to the dimensions of the fixed-length apparatus and the most favourable dimensions of the variable-length apparatus, errors of less than $0\cdot 5\%$ occur in calculating λ (hence D_T/μ) from R using equation (4) when $D_L/D_T\sim 1$ except when R is less than about $0\cdot 2$ and the measurement of the current ratio becomes in any case less accurate. On the other hand, some of the measurements reported in this paper required the use of the variable apparatus with $h=5$ cm. In this case, under certain circumstances the term $\frac{1}{2}-(D_L/D_T)(b/d)^2$ is no

longer negligible, and equation (3) rather than (4) should be used.

For $E/N \geq 60$ Td in D_2 and $E/N \geq 100$ Td in CO the divergence of the electron stream becomes significantly affected by longitudinal electron density gradients caused by ionisation. The formula for the current ratio required to analyse the data in these circumstances is

$$R \approx 1 - \left\{1 + \left(\tfrac{1}{2} - \frac{D_L}{D_T}\right)\left(\frac{b}{d}\right)^2\right\}\frac{h}{d}\exp\left\{-\lambda\left(1 - \frac{\alpha_T}{\lambda_L}\right)(d-h)\right\}, \quad (5)$$

where α_T is Townsend's first ionisation coefficient and $\lambda_L = \nu_{dr}/2D_L$ (Huxley and Crompton 1974). Thus, when ionisation is significant, a small fractional correction α_T/λ_L must be made to the values of D_T/μ calculated from the current ratio R using either equation (3) or (4).

The basic modification to each of the apparatuses from the form in which they were used for the most recently published measurements of D_T/μ from these laboratories was the replacement of the radioactive α-particle emitter as the source of electrons by a thermionic emitter. This was necessary in order to eliminate negative ions produced by the radioactive sources through dissociative attachment in the experiments with CO.

Experiments were carried out in a series of short intervals to reduce the heating of the gas by the filament. The gas pressure was monitored continuously and measurements were discontinued when a pressure change of more than 0·2–0·3% was observed. As a test of the procedure, measurements were performed in pure hydrogen. The results obtained were in excellent agreement (to within ±0·5%) with previously published results (see Huxley and Crompton 1974).

A test of the dependence of the results on the apparatus geometry was made with CO using the variable-length apparatus with cathode–anode separations of 5 and 10 cm. The agreement between the results obtained using the two lengths, and between these results and those from the fixed-length apparatus with its superior dimensional accuracy, can be seen in Table 3 below. The dependence of the results on the total electron current was tested by varying the current (usually of the order of 10^{-12} A) by a factor of 10.

(c) Gas Handling

Carbon monoxide. Under certain conditions, Haddad and Milloy (1983) reported large background currents due to negative ions in their drift velocity experiments which prevented them from making measurements at pressures greater than 1 kPa and E/N less than 10 Td. Mass spectrometric analysis of the gas from the cylinder of CO (Matheson Research Grade) used by them revealed that low levels of impurity were present which apparently did not affect their values of ν_{dr} (except perhaps at $E/N = 10$ Td—see Section 4) but were the major source of the background. Two new cylinders of gas (quoted purity 99·99%) were purchased from the same supplier which proved to have much lower levels of impurity. Gas from these cylinders was therefore used for all our measurements. Some problems with negative ion backgrounds remained (see Section 4) but they were much reduced.

Table 1. Values of D_T/μ (in volts) in CO at 293 K for $E/N \geq 10$ Td measured in the variable-length apparatus using lengths of 5 and 10 cm to obtain the most favourable current ratios

E/N (Td)	p (kPa) 0·1333	0·2667	0·6667	1·333	Average
120*	1·631	1·630			1·631
100	1·377	1·380			1·379
90	1·269	1·267			1·268
80	1·170	1·170			1·170
70	1·094	1·091			1·093
60	1·030	1·030	1·030		1·030
55		1·003	1·004		1·003
50	0·978	0·976	0·977		0·977
45		0·947	0·947		0·947
40		0·913	0·913		0·913
35		0·873	0·873	0·873	0·873
30		0·823	0·822	0·823	0·823
25		0·7587	0·7589	0·7597	0·759
20		0·6802	0·6785	0·6785	0·679
15		0·5738	0·5720	0·5716	0·573
12			0·4860	0·4882	0·487
10			0·4281	0·4274	0·428

* Correction due to longitudinal diffusion was not made and is uncertain.

Table 2. Values of D_T/μ (in volts) in CO at 293 K for $E/N \geq 10$ Td measured in the apparatus with thick guard rings, together with the best estimates derived from the data from both apparatuses

The best estimates take account of the more favourable conditions under which the results for $E/N \geq 25$ Td were taken in the variable-length apparatus

E/N (Td)	p (kPa) 0·1333	0·2667	0·6667	1·333	Average	Best estimate from both data sets
120*	1·628					1·631
100*	1·387					1·380
90*	1·273					1·270
80*	1·174					1·171
70*	1·096					1·094
60*	1·032	1·032			1·032	1·030
55*		1·003				1·003
50*		0·977				0·977
45*		0·949				0·948
40*		0·916				0·914
35*		0·874				0·873
30*		0·820				0·823
25*			0·7591			0·759
20			0·6800	0·6800	0·6800	0·680
17			0·6204	0·6204	0·6204	0·620
15			0·5728	0·5727	0·5728	0·573
14			0·5479	0·5476	0·5478	0·548
12			0·4910	0·4911	0·4910	0·491
10			0·4276	0·4281	0·4279	0·428

* Results at these values of E/N were obtained with low current ratios.

Deuterium. Gas of high purity was prepared by passing deuterium of the highest purity available commercially through a silver palladium osmosis tube. It is believed that the only impurity present at a significant level was hydrogen and that the abundance of H_2 did not exceed 0·5% (see Crompton and Elford 1962; McIntosh 1966).

4. Results and Discussion

(a) Carbon Monoxide

The ratio D_T/μ. Impurities in the samples of CO from the new cylinders (see Section 3) were still found to affect the results, as shown by their time dependence after a new sample of gas was admitted to the apparatus. It was found that purification could be achieved either by the gettering action of the hot filament over a long period (24 hours typically) or by purifying the gas in a liquid nitrogen trap. Values obtained by both techniques turned out to be identical and the latter technique of purification was adopted for the final measurements.

Table 3. Values of D_T/μ (in volts) in CO at 293 K for $E/N \leq 10$ Td obtained using both apparatuses

E/N		Variable length			Fixed length		Best
(Td)	p (kPa)	1·333	1·333	0·667	1·333	0·667	estimate
	h (cm)	10	5	5	10	10	
10		0·427	0·427	0·428	0·428	0·428	0·428
9			0·392		0·392	0·394	0·393
8		0·356	0·358	0·358	0·358	0·358	0·358
7		0·319					0·319
6		0·282			0·285		0·284
5		0·244	0·245	0·246	0·245	0·245	0·245
4		0·208			0·209		0·209
3·5		0·1902					0·1902
3·0		0·1730	0·1721		0·1728	0·1728	0·1728
2·5		0·1559					0·1559
2·0		0·1385			0·1380	0·1385	0·1384
1·7		0·1278					0·1278
1·4		0·1167					0·1167
1·2		0·1077					0·1077
1·0		0·0985			0·0983		0·0984

Tables 1 and 2 show the results for $10 \leq E/N \leq 120$ Td obtained in the two apparatuses, while Table 3 shows the results for $E/N \leq 10$ Td. That the results were not dependent on the pressure p can be seen from Tables 1 and 2. Each experimental value is an average of between 5 and 10 experimental results obtained with at least three different samples of gas. As discussed in Section 3, the results shown in Table 3 are presented in order to demonstrate the independence of the results on apparatus geometry.

Above 30 Td the measurements in the fixed-length apparatus could only be made under conditions where the current ratios were regarded as too small for accurate measurement. These results are therefore marked with an asterisk in Table 2. By reducing the cathode–anode spacing of the variable-length

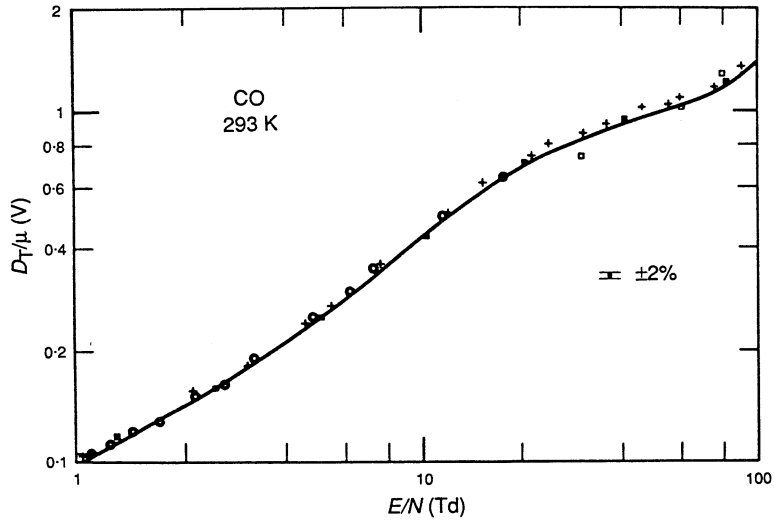

Fig. 1. Experimental results for D_T/μ in CO: —— present results; ■ Skinker and White (1923); O Warren and Parker (1962); □ Lakshminarasimha *et al.* (1974); + Roznerski and Mechlinska-Drewko (1979). For error bounds, see Section 4*a*.

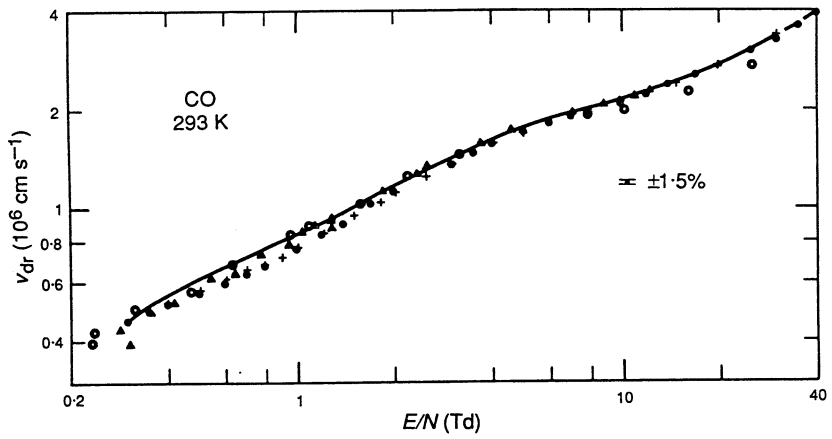

Fig. 2. Experimental results for v_{dr} in CO: —— present results; O Pack *et al.* (1962); ▲ Wagner *et al.* (1967); --- Haddad and Milloy (1983); + Roznerski and Leja (1984); ● Nakamura (1987). For error bounds, see Section 4*a*.

apparatus to 5 cm, measurements could be made with at least two pressures up to 120 Td (see Table 1).

It was not possible to purify the gas samples adequately above 1·333 kPa due to the small capacity of the liquid nitrogen trap used to purify the gas samples prior to admitting them to the apparatus. The results for $E/N \leq 10$ Td shown in Table 3 were therefore obtained only at the pressures shown. Furthermore, at higher pressures variation of the gas pressure due to heating

by the filament was greater than the acceptable 0·2% over the period necessary for the measurements.

The Huxley formula was used to derive D_T/μ values from the current ratios over the entire range of E/N. For $E/N = 100$ Td, which is the highest value of E/N where the data for D_L derived by Lowke and Parker (1969) are available, the correction for longitudinal diffusion was found to be only 0·3%; the data above $E/N = 100$ Td were not corrected for either longitudinal diffusion or ionisation.

The estimated uncertainty of the data is less than ±2%. This value includes possible overestimates of the uncertainty due to the presence of impurities and thermal effects (for which 0·5% was assigned), as well as the statistical scatter of the data which was less than 0·5%. (Note that thermal effects are one of the contributers to the statistical scatter.)

Table 4. Drift velocities (in units of 10^6 cm s^{-1}) in CO at 293 K

Values in parentheses may be subject to a small additional error due to less favourable experimental conditions (see Section 4*a*)

E/N	v_{dr} measured at p (kPa) of								Best
(Td)	0·413	0·723	1·033	2·066	4·00	6·61	8·06	13·43	estimate
25	3·008								(3·008)
20	2·708								(2·708)
17	2·527								(2·527)
14	2·347	2·351							2·349
12	2·227	2·231	2·231						2·230
10	2·107	2·111	2·110						2·106
8	1·982	1·983	1·984						1·983
7	1·912	1·914	1·914						1·913
6	1·830	1·833	1·833						1·832
5		1·734	1·735	1·734					1·734
4		1·604	1·603	1·603					1·603
3·5		1·522	1·521	1·520					1·521
3			1·422	1·421					1·422
2·5			1·305	1·304	1·305				1·305
2·0			(1·170)	1·168	1·169				1·169
1·7			(1·078)	1·075	1·076	1·078			1·077
1·4				0·975	0·976	0·978	0·977		0·977
1·2				0·906	0·906	0·907	0·907		0·907
1·0					(0·832)	0·834	0·834		0·834
0·8						0·759	0·758		0·758
0·7						0·718	0·718		0·718
0·6						0·673	0·673		0·673
0·5						0·619	0·620		0·620
0·4							0·549	(0·545)	0·549
0·35							0·504	(0·505)	0·504
0·30							(0·452)	(0·453)	(0·452)

The results of the present measurements over the full range of E/N are shown in Fig. 1 where they are compared with earlier data. Our results are in good agreement with other published experimental data below 20 Td (Skinker and White 1923; Warren and Parker 1962), but at moderate values of E/N there is a difference of up to 5% with the data of Roznerski and Mechlinska-Drewko

(1979); the older data of Skinker and White agree with our data somewhat better.

Drift velocities. A background current of negative ions made the measurements difficult only when pressures greater than about 13 kPa were used. Using pressures less than this value it was possible to extend the measurements down to 0·3 Td, in contrast to the situation in the Haddad and Milloy experiments where the background, and the limitation to the pressure caused by it, prevented them making measurements below 10 Td.

The results are shown in Fig. 2 and in Table 4. The estimated error bounds are ±1·5%. These error limits are somewhat higher than in other drift velocity measurements due to the diffusion correction being sometimes as large as 0·7% at the lowest pressures, and due to the presence of the ionic background current at the highest pressures. These effects somewhat degrade the accuracy of the measurements at the highest and lowest values of E/N. However, most of the data were obtained under more favourable conditions and therefore the suggested error bounds are thought to be conservative. An uncertainty of ±1% is a more realistic estimate for the majority of the data.

The present results are in good agreement with those of Pack *et al.* (1962), except at the three highest values of E/N where their data are up to 10% lower, and with the data of Wagner *et al.* (1967) with the exception of a few points below 2 Td where the scatter in their data is between 5 and 10%. On the other hand, the results of Roznerski and Leja (1984) are lower than the present data and the data of Pack *et al.* by up to 12% below 6 Td. More recent measurements by these authors (Roznerski, personal communication) have led to an improved agreement. The agreement of the present results with the data of Haddad and Milloy in the range of overlap is better than 0·3% except at 10 Td where the difference is 1%. The recent results of Nakamura (1987) agree well with the present results above 2 Td, but diverge in the range 0·35 to 2 Td. In this range they agree well with the data of Roznerski and Leja and therefore disagree with the present results by up to 11%. This difference is unacceptably large given the claimed precision of the measurements (±1% for Nakamura's and better than ±1·5% for the present) and requires further investigation.

Vibrational excitation cross sections. A comparison of our new experimental data for D_T/μ with values calculated using the Haddad and Milloy (1983) cross sections shows that some modifications to their cross sections are required. This is to be expected given the discrepancies between the calculated and measured values of D_T/μ shown in Fig. 2*b* of the Haddad–Milloy paper and the fact that our data generally agree remarkably well with the data used for the earlier comparison. Now, as previously, the differences occur mainly at the lower values of E/N, the region mostly affected by non-resonant vibrational excitation. Although we were able to fit the D_T/μ data, without destroying the fit to the ν_{dr} data for the pure gas and the mixtures, by appropriate adjustments to the non-resonant 'foot' of the vibrational cross section and to the momentum transfer cross section, we do not feel justified in presenting modified cross sections for this energy range because of the lack of uniqueness caused by the large number of rotational excitation cross sections, the rapidly changing momentum transfer cross section, and the proximity of the large resonance in the vibrational cross section. On the other hand, we found it

necessary to make only a small adjustment to the scaling factor (from 1·30 to 1·35) for the resonant part of the cross section to obtain an adequate fit to the D_T/μ data. This adjustment, accompanied by a small adjustment to the cross section for excitation of the $a^3\pi$ state, could also be made without significantly affecting the fit to the mixture data. The modification to the normalisation factor for the vibrational cross section in the resonance region is within the error bounds that might reasonably be assigned to the factor determined by Haddad and Milloy.

(b) Deuterium

The ratio D_T/μ. Because the majority of the measurements in deuterium were to be made in a range of E/N for which the fixed-length apparatus was unsuitable, all of them were made using the variable-length apparatus. Prior to the commencement of the measurements a fault developed that required the apparatus to be rebuilt. In the process a low resistance developed between the outermost annulus of the anode and ground making the measurements more difficult to perform, although it would not have affected their accuracy. It was therefore decided to make the measurements with this section earthed. Thus, the current ratios R' that were measured in this set of experiments were ratios of the current to the central disk of radius 0·5 cm to the total current received by that disk and the surrounding annulus of outer radius 2·0 cm (Crompton and Jory 1962).

Under some circumstances not all the current fell on this area. The data therefore had to be analysed differently to take account of this. The maximum divergence of the stream can be judged from the fact that the maximum current falling outside the collecting area of 2 cm radius was only 11%. Under most conditions, i.e. when $R' \geq 0{\cdot}2$ (the conditions for accurate measurement of the current ratio), less than 1% fell outside this area.

The Huxley formula was used to calculate the values of D_T/μ presented in Table 5. Results were obtained for a number of pressures and for two drift lengths (5 and 10 cm). The range of current ratios for each pressure is also shown in the table. The results were expected to be somewhat less accurate than normal when R' fell below 0·2. However, the good agreement between results taken under these conditions and those taken under more favourable conditions suggests that this criterion is somewhat conservative. The results in parentheses in Table 5 were taken to demonstrate this point.

Because many of the results presented in Table 5 were taken with $h = 5$ cm it was necessary to determine whether anisotropic diffusion could affect the interpretation of the results (see Section 3). The ratios D_L/D_T required in order to apply equation (3) were calculated using the theory of Lin *et al.* (1979) and checked with predictions based on the generalised Einstein relations (see Robson 1972, 1976, 1984). The two approaches gave results that were in good agreement and indicated that above 40 Td the ratio becomes greater or equal to 1, while below 40 Td it suddenly decreases to around 0·5. Thus, from around 40 Td upwards, the results might be expected to show some inconsistencies when analysed with the simple Huxley formula, particularly those taken at lower pressures. However, rather surprisingly, the results shown in Table 5

Table 5. Values of D_T/μ (in volts) in D_2 at 293 K measured in the variable-length apparatus

The results obtained with current ratios less than 0·2 are shown in parentheses. Values shown here for $E/N \geq 70$ Td have not been corrected for the effect of ionisation

E/N		McIntosh (1966)[A]	Results obtained using indicated values of *h* and *p*									Average
(Td)	*p* (kPa)		2·066	1·343	1·033	0·723	2·066	1·033	0·723	0·413	0·3306	
	Current ratios		0·3–0·4	0·25–0·3	0·20–0·25	0·15–0·25	0·5–0·7	0·4–0·5	0·3–0·4	0·25–0·3	0·2–0·3	
	h (cm)	10	10	10	10	10	5	5	5	5	5	
100										2·90	2·90	2·90
80										2·63	2·63	2·63
70										2·49	2·49	2·49
60										2·33	2·33	2·33
50									2·14	2·14	2·14	2·14
40									1·878	1·872	1·877	1·876
35								1·698	1·696	1·695	1·698	1·697
30								1·476	1·472	1·474	1·472	1·474
25						1·229		1·232	1·229	1·228	1·231	1·230
20						1·006		1·007	1·004	1·007		1·006
17					0·886	0·887	0·889	0·889	0·887	0·886		0·887
14					0·770	0·774	0·774	0·774	0·772			0·773
12				0·695	0·695	0·697	0·697	0·696	0·696			0·696
10				0·615	0·614	0·615	0·616	0·616	0·614			0·615
8			0·530	0·529	0·530	(0·530)	0·531	0·530				0·530
7			0·485	0·485	0·484	(0·484)	0·486	0·485				0·485
6		0·437	0·436	0·436	0·438	(0·437)	0·438					0·437
5		0·388	0·388	0·387		(0·388)	0·388					0·388
4		0·334	0·334				0·334					0·334
3·5		0·305	0·305				0·306					0·305
3·0		0·275	0·274									

[A] Interpolated values.

(calculated using equation 4) show no dependence on either pressure or the value of h. On the other hand, when equation (3) rather than (4) was used to analyse the data the values of D_T/μ between 40 and 100 Td showed a small pressure dependence (<1%), and were larger by up to 2%. This pressure dependence suggests that the data calculated in this way may be less accurate than those calculated using the Huxley formula. Therefore it was decided to use the results calculated with the latter but, since the only preference for these results, derived from a less soundly based formula, was their greater consistency, the upper error bound has been increased by 2%.

Table 6. Corrections to the values of D_T/μ in D_2 due to ionisation for $E/N \geq 50$ Td together with the final values

E/N (Td)	α_T/λ_L (%)	Final values (V)	E/N (Td)	α_T/λ_L (%)	Final values (V)
100	1·40	2·86	60	0·20	2·33*
80	0·80	2·61	50	0·09	2·14*
70	0·60	2·48			

* To the accuracy quoted these values are unchanged.

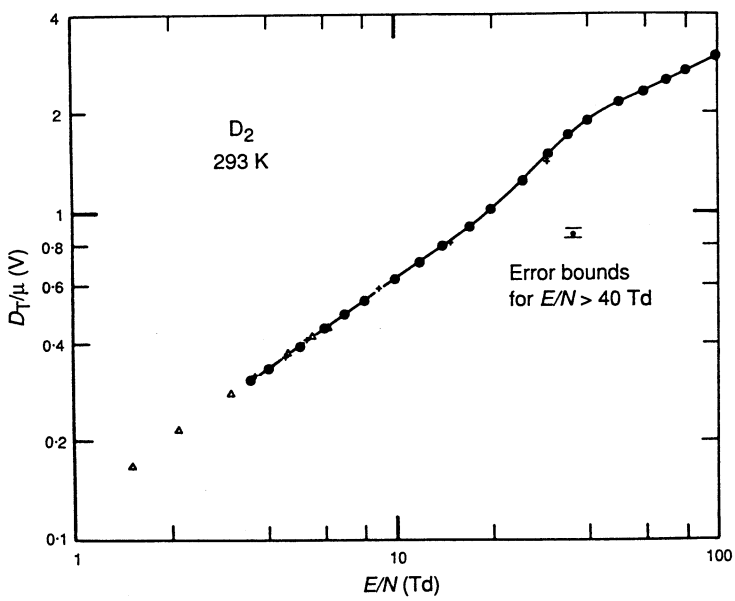

Fig. 3. Experimental results for D_T/μ in D_2: —●— present results; + Hall (1955); △ McIntosh (1966). For error bounds, see Section 4*b*; the maximum uncertainty (–1·5 to +3·5% above $E/N = 40$ Td) is as indicated.

At the higher values of E/N where $\alpha_T \neq 0$ it is necessary to apply a correction for ionisation to the values of D_T/μ calculated by using equation (3) or (4). As shown in Section 3, the fractional correction to be applied is α_L/λ_L and is independent of pressure.

Values for α_T were initially taken from Buckman and Phelps (1985). It was assumed that the values of α_T for their D_2–CO mixture with 0·2% of CO are not significantly different from the coefficients for pure deuterium. The calculated corrections are given in Table 6 together with the final values for D_T/μ that were affected by this correction.

The reproducibility of the data shown in Table 5 was to within ±0·2% and therefore the error bars can be estimated (Huxley and Crompton 1974) as ±1% from 3·5 to 25 Td, ±1·5% from 25 to 35 Td, and +3·5 to −1·5% from 40 to 100 Td.

Our results are shown graphically in Fig. 3. There is good agreement in the range of overlap with the data of Hall (1955), McIntosh (1966) and Crompton *et al.* (1968). Where they overlap, the results of Warren and Parker (1962) differ by 5 to 7%. [For an assessment of the data of Warren and Parker see Crompton *et al.* (1968).]

Table 7. Drift velocities (in units of 10^6 cm s^{-1}) in D_2 at 293 K

The raw data have been corrected for the effects of diffusion (see Section 4*b*)

E/N (Td)	McIntosh (1966) (interpolated)	v_{dr} measured at *p* (kPa) of 1·343	0·723	0·413	Best estimate
30				3·37	3·37
25			2·89	2·89	2·89
20			2·49	2·48	2·49
17			2·25	2·25	2·25
14	2·02	2·01	2·01	2·01	2·01
12	1·847	1·846	1·846	1·846	1·846
10	1·669	1·671	1·668		1·669
8	1·480	1·480	1·479		1·480
7	1·378	1·379	1·377		1·378
6	1·270	1·271	1·270		1·270
5	1·154	1·155			1·155
4	1·028	1·029			1·029
3·5	0·961	0·961			0·961
3	0·888	0·888			0·888

Drift velocities. By making some measurements at pressures somewhat lower than those used by McIntosh (1966) (our pressure was 0·413 kPa compared with his 0·667 kPa) we were able to extend our measurements to 30 Td. Above this value of *E/N* at the pressure of 0·413 kPa electrical breakdown occurred. If the pressure was lowered still further in an attempt to reach higher values of *E/N* the efficiency of the electrical shutters was reduced, preventing any reliable measurements even at 25 and 30 Td.

The results are shown in Table 7. The maximum correction for diffusion was 0·8%, and the maximum scatter of the data was ±0·2%. Therefore, the total uncertainty is estimated to be ±1·5% between 17 and 30 Td.

The results are shown graphically in Fig. 4 where they are compared with earlier data. In the range of overlap the present results are in excellent agreement with those of McIntosh (1966). The data of Crompton *et al.* (1968) taken at 77 K (not shown in the figure) are also in agreement with the present results at their highest values of *E/N* where the gas temperature has little influence. The somewhat older results of Pack *et al.* (1962) are larger than

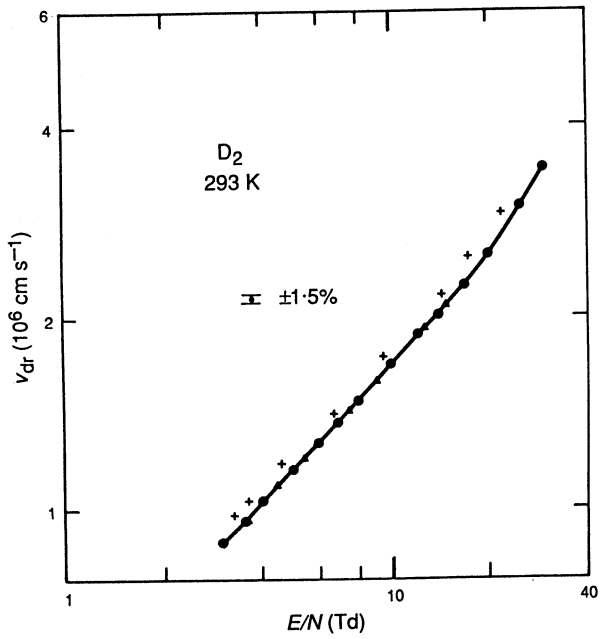

Fig. 4. Experimental results for v_{dr} in D_2: —●— present results; + Pack *et al.* (1962); ▲ McIntosh (1966). For error bounds, see Section 4*b*.

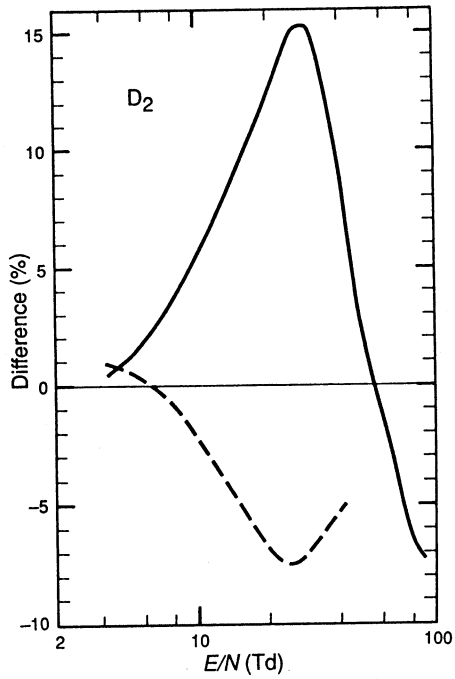

Fig. 5. Differences between the present experimentally determined values of D_T/μ and v_{dr} for D_2 and those calculated using the set of cross sections determined by Buckman and Phelps (1985) that best matched their excitation rate coefficient data: —— D_T/μ; --- v_{dr}.

ours. Similar discrepancies between the data of Pack *et al.* and the data from our laboratory exist for hydrogen. It appears that there are no other high precision measurements of ν_{dr} for D_2 in the range of E/N of our measurements except the very recent ones of Roznerski *et al.* (1987) which are also in very good agreement with our data.

Vibrational excitation cross sections. Buckman and Phelps (1985) found that they were unable to derive a set of cross sections that were consistent with all of the available transport coefficient data for D_2 and their own experimental data for the $\nu_0 = 1$ to $\nu = 1$ excitation coefficient. They therefore derived two sets, and commented that the somewhat larger vibrational cross section of the set that gave best agreement with the excitation coefficient data led to differences as large as 12% with existing data for D_T/μ in the range $10 \leq E/N \leq 100$ Td. Unfortunately, our new data do not significantly alter this picture. Fig. 5 shows the extent of the mismatch between calculated and measured transport coefficients when the set of cross sections proposed by Buckman and Phelps as best fitting the rate coefficient data are used for the calculations. For a range of values of E/N about 30 Td where the disagreement is a maximum, the differences are many times the experimental uncertainty of the present measurements. This is a problem that clearly requires resolution, yet as argued by Buckman and Phelps it is not easy to see where the solution may lie.

5. Conclusions

Drift velocities and D_T/μ ratios have been measured for carbon monoxide and deuterium over a range of values of E/N where high accuracy data were previously lacking and vibrational excitation is the major inelastic process determining the transport data. These data will fill the need for transport coefficient data for gas discharge modelling and for determining or normalising electron scattering cross sections. For both gases, however, more data are required from both beam experiments and theory, and the range of E/N covered by swarm experiments requires further extension, before a single, unique set of cross sections can be obtained. Even so, it appears that an understanding of the apparent incompatibility between the results of the two types of swarm experiment in D_2, as illustrated by Fig. 5, may require more than some additional experimental data.

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