Aust. J. Phys., 1990, **43**, 755–63

The Drift Velocity of Electrons in Water Vapour at Low Values of *E/N*

B. Cheung and M. T. Elford

Atomic and Molecular Physics Laboratories, Research School of Physical Sciences, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia.

Abstract

The drift velocity of electrons in water vapour at 294 K has been measured over the *E/N* range 1·4 to 40 Td with an error estimated to be $\leq \pm 0 \cdot 5\%$ for $5 < E/N\,(\mathrm{Td}) < 35$ and $\pm\, 0 \cdot 7\%$ for $E/N < 5$ Td and $E/N > 35$ Td. The present data show that μN decreases monotonically with decreasing *E/N* at low *E/N* values as observed by Wilson *et al.* (1975) and does not become independent of *E/N* as indicated by Lowke and Rees (1963). The present values, although lower than those of Lowke and Rees, lie within the combined error limits, except for values below 2 Td. The present data suggest that the momentum transfer cross section at low energies is approximately 10% larger than that obtained by Pack *et al.* (1962) from their drift velocity measurements.

1. Introduction

The analysis of electron transport coefficients to derive information on energy dependent cross sections for electron scattering processes in water vapour (e.g. Ness and Robson 1988) requires data of high accuracy. One of these coefficients is the drift velocity v'_{dr}. There appear to have been four sets of drift velocity data published for water vapour since 1962 (Pack *et al.* 1962; Lowke and Rees 1963; Ryzko 1966; Wilson *et al.* 1975). Although the data of Lowke and Rees, which cover the *E/N* range 1 to 46 Td (*E* is the electric field strength and *N* the gas number density; $1\ \mathrm{Td} \equiv 10^{-17}\ \mathrm{V\,cm^2}$), are generally considered the most reliable in this *E/N* range with a stated error of $\leq \pm 2\%$ (Gallagher *et al.* 1983), they are anomolous in that the values of μN (where $\mu = v'_{\mathrm{dr}}/E$ is the electron mobility) are independent of *E/N* between 2 and 20 Td. The later measurements of Wilson *et al.* (1975) indicate that μN decreases monotonically with decreasing *E/N* over this *E/N* range. By obtaining drift velocity data of higher accuracy than those obtained in previous studies it has been possible in the present work to re-examine the variation of μN with *E/N* over this low *E/N* region, as well as provide improved data for the study of cross sections.

0004-9506/90/060755$03.00

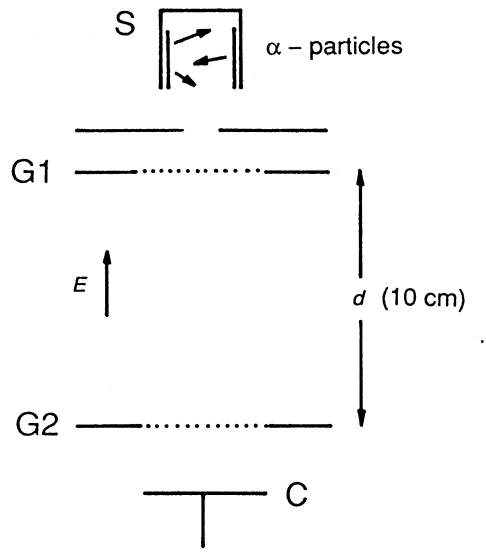

Fig. 1. Schematic diagram of the drift tube: G1 and G2 are Bradbury–Nielsen shutter grids, S is the electron source and C the collector.

2. Apparatus and Experimental Technique

(a) Apparatus

The drift velocity was measured using the Bradbury–Nielsen time-of-flight method. The apparatus (shown schematically in Fig. 1) and the experimental procedures have been described in detail by Elford (1972) and Huxley and Crompton (1974) and therefore will be only briefly considered here. The electrons were produced by the ionisation of water molecules by α-particles from an ^{241}Am foil. Since the primary electron produced in the ionising event has an energy of approximately 30 eV a significant number of negative ions are also formed in the source by dissociative attachment.

The distilled water used was deionised and care taken to remove dissolved air by vacuum degassing. This procedure prevented the formation of negative ions by electron attachment to oxygen and thus a reduction in the available electron currrent. At frequent intervals the water vapour was frozen and any permanent gases pumped off. The drift tube operated in a water bath in order to ensure the temperature varied by less than 0·1 K per hour.

The ions and electrons are gated into the drift space of length d (100·0 mm in this work) by a Bradbury–Nielsen shutter grid G1 operated by a sinusoidal signal. The second grid G2, identical to G1, is operated by a sinusoidal signal of the same phase and amplitude as that supplied to G1. A typical 'arrival time spectrum', obtained by measuring the current transmitted to the collector C as a function of the frequency of the sinusoidal signal, is shown in Fig. 2, the current maxima occurring at frequencies f^n ($n = 1, 2, 3, \ldots$ is the peak order number), which are integral multiples of the frequency, f^1, at which the first order current maximum occurs. The measured drift velocity v_{dr}' is then given

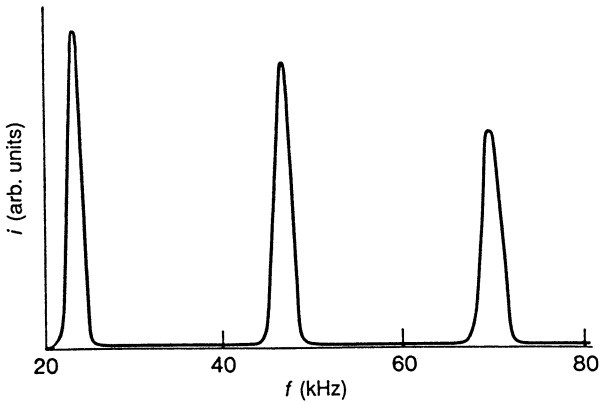

Fig. 2. Typical current–frequency curve (i.e. arrival time spectrum). The experimental conditions were 1·058 kPa and 20 Td. All data points lie within the thickness of the line.

by $v'_{dr} = f^n/nd$, where d is the drift length. An automated control and data acquisition system was used to derive the frequencies f^n corresponding to the current maxima.

The vapour pressures used ranged from 0·496 to 1·343 kPa and were measured using a calibrated capacitance manometer (MKS Baratron Type 94AM-10SP). Deviations from the perfect gas law used to calculate the number density N were less than 0·1% at the highest pressure used. The upper limit to the pressure range, 1·343 kPa, was set by the presence of a large leakage current due to the presence of water films on insulators.

(b) Effect of Shutter Open Time

The electron currents available from the source at the relatively low pressures used were very small since the current from the radioactive source is proportional to the pressure. It was therefore necessary under some circumstances to use relatively large shutter open times in order to ensure that the transmitted current was sufficient for accurate measurement. Under these conditions the values of v'_{dr} were found to be a function of the shutter open time. Since the open time is inversely proportional to both the value of n and to the amplitude of the shutter signal V_0, the value of v'_{dr} corresponding to zero open time was obtained by plotting v'_{dr} as a function of $(nV_0)^{-1}$ and extrapolating to zero.

(c) Diffusion and End Effects

In many drift velocity measurements end effects and diffusion cause v'_{dr} to be a function of the gas number density (Elford 1972). The usual correction

procedure is to represent the dependence by the relation

$$v'_{dr} = v_{dr}\,(1 + C/N),$$

where C is a constant for a given value of E/N and gas temperature. The true drift velocity v_{dr} is obtained by plotting v'_{dr} as a function of $1/N$ and extrapolating to zero $1/N$. In the present work the measured drift velocities were found to be independent of number density to within the experimental scatter and thus no corrections were required.

(d) Background Currents

At values of $E/N < 5$ Td, where the current available was particularly small, the very large shutter open times required (i.e. low values of V_0) resulted in a large background current and increased error in the extrapolation to zero open time. The upper limit to the E/N range was set by the presence of a large background current caused, in this case, by the failure of the shutters to prevent the transmission of electrons regardless of the value of V_0. However, at intermediate values of E/N, no background was observed. Since the source is known to produce negative ions, the absence of a background was surprising since it has generally been assumed that the presence of negative ions gives rise to a background current which increases with frequency (Elford 1972).

The first step in determining the reason for the absence of a background current was to check that negative ions did in fact reach the first grid G1. This was done by operating the shutter G1 as an 'inverse Loeb filter' (Elford 1986). The plot confirmed that a significant negative ion current reached this grid. In order to study the transmission characteristics of grid G1 for ions under operating conditions (i.e. with sine wave signals applied), the current transmitted by this shutter was measured as a function of frequency (at a constant signal amplitude). It was not possible to obtain an unambiguous result for this test by using negative currents because of the presence of both electrons and negative ions. However, since positive ions have mobilities which are similar to those of negative ions, it is probable that their transmission characteristics for a Bradbury–Nielsen shutter are similar. The polarity of the potentials applied to the drift tube was therefore reversed and positive ions extracted from the source.

With the shutter signal amplitude normally used in the measurements (30 V peak to peak), it was found (Fig. 3) that at 1·33 kPa and 25 Td there was no detectable positive ion current transmitted by the shutter at frequencies between 20 and 400 kHz, which was the range over which the electron current spectrum was observed. The form of this transmission curve can be explained by the low drift velocity of ions in water vapour. Above 400 kHz the time between successive shutter openings (i.e. the half period) is too small for all the ions to be deflected and collected on the wires and thus the shutter never actually shuts. Below 400 kHz the shutter operates in trapping the ions when shut, but above 20 kHz the shutter is not open sufficiently long for the ions to be transmitted and move away from the immediate vicinity of the shutter wires before the shutter closes and the ions are again collected on the wires. Note that if a much lower value of V_0 is used (say 10 V, peak to peak, Fig. 3),

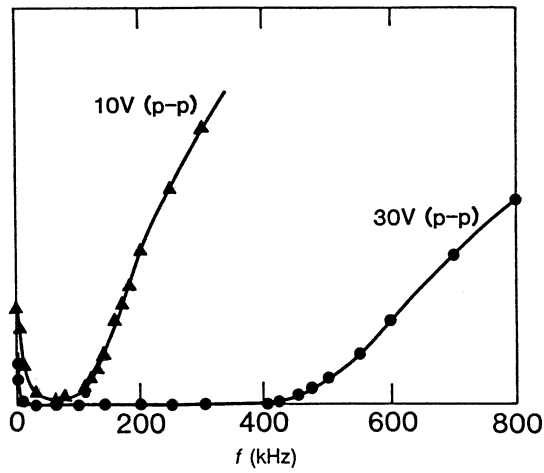

Fig. 3. Current transmitted by shutter G1 as a function of the signal frequency for two values of the signal amplitude. The pressure and E/N values were 1·33 kPa and 25 Td.

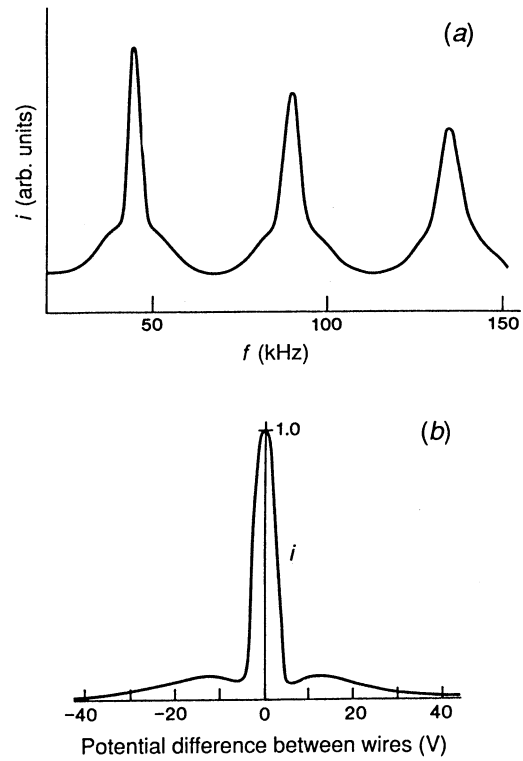

Fig. 4. (*a*) Arrival time spectrum obtained at 1·334 kPa and 35 Td showing subsidiary maxima. (*b*) Variation of the transmitted current as a function of the potential difference between adjacent shutter wires (i.e. a 'cut-off' curve) for the same experimental conditions.

ions are transmitted at all frequencies. Since the transmission increases with frequency a background current which rises with frequency will be observed in the arrival time spectrum. It appears that the lack of transmission of positive (and presumably) negative ions over the frequency range 20 to 400 kHz (with a V_0 value of 30 V, peak to peak) is specific to water vapour. When hydrogen was used instead of water vapour under the same experimental conditions there was a significant transmitted positive ion current.

(e) Distortion of Current Maxima

The arrival time spectra at high values of E/N show an interesting distortion in that the maxima have subsidiary small wings on either side (Fig. 4*a*). This effect arises from the transmission characteristics of the shutters as measured by a plot (termed a 'cut-off' curve) of the fraction of the current transmitted by a shutter grid as a function of the dc potential between adjacent shutter wires. The 'cut-off' curve taken under the same experimental conditions as that for the arrival time spectrum of Fig. 4*a* is shown in Fig. 4*b*. Because of the relatively small effect of diffusion under these conditions, the transmission characteristics of the shutters are reflected in the spectrum. Similar effects have been observed by England and Elford (1988) in drift velocity measurements in H_2–Kr mixtures.

(f) Experimental Checks

The measured drift velocities were stable to within the experimental scatter (<±0·1 to 0·2%) over periods of many hours indicating that effects from outgassing were negligible. As a check on the accuracy of the experimental

Table 1. Drift velocity of electrons in water vapour at 294 K

Entries are in cm s^{-1} unless stated otherwise

E/N	p (kPa)				Best est.	μN
(Td)	0·496	0·723	1·058	1·343	(average)	(10^{23} V^{-1} cm^{-1} s^{-1})
1·4				3·158×10^4	3·158×10^4	2·256
1·7		3·851	3·847	3·840	3·846	2·262
2·0		4·523	4·512	4·512	4·516	2·258
2·5		5·646	5·641	5·643	5·643	2·257
3·0	6·797	6·780	6·772	6·797	6·786	2·262
3·5	7·948	7·935	7·926	7·943	7·938	2·268
4·0	9·054	9·054	9·038	9·056	9·051	2·263
5·0	1·131×10^5	1·130×10^5	1·130×10^5	1·131×10^5	1·130×10^5	2·260
6·0	1·358	1·363	1·360	1·358	1·359	2·266
7·0	1·589	1·591	1·590	1·591	1·590	2·272
8·0	1·818	1·818	1·820	1·820	1·819	2·274
10·0	2·280	2·277	2·280	2·277	2·279	2·279
12·0	2·743	2·747	2·743	2·741	2·744	2·286
14·0	3·215	3·215	3·212	3·213	3·214	2·295
17·0	3·937	3·934	3·931	3·930	3·933	2·314
20·0	4·671	4·666	4·664	4·668	4·667	2·333
25·0	5·997	6·000	5·981	5·975	5·988	2·395
30·0	7·408	7·389	7·392		7·396	2·465
35·0	9·005	8·999	9·033		9·012	2·575
40·0	1·134×10^6	1·135×10^6			1·135×10^6	2·836

system, a series of measurements were made of the drift velocity of electrons in hydrogen. The values obtained agreed in all cases with previous values taken in this laboratory (Elford and Robertson 1973) to within 0·2%.

3. Results

The measured drift velocities at 294 K are shown in Table 1 as a function of both E/N and pressure. As noted earlier the absence of a dependence on pressure indicates that end effects and diffusion may be regarded as negligible. The best estimate values of v'_{dr}, obtained by averaging the data at a given value of E/N, were converted to values of μN (see Table 1) and plotted in Fig. 5*a* as well as on an expanded scale at low E/N values in Fig. 5*b*. The errors in the present values are listed in Table 2. The total errors were found by adding the systematic errors in quadrature and then the random error arithmetically.

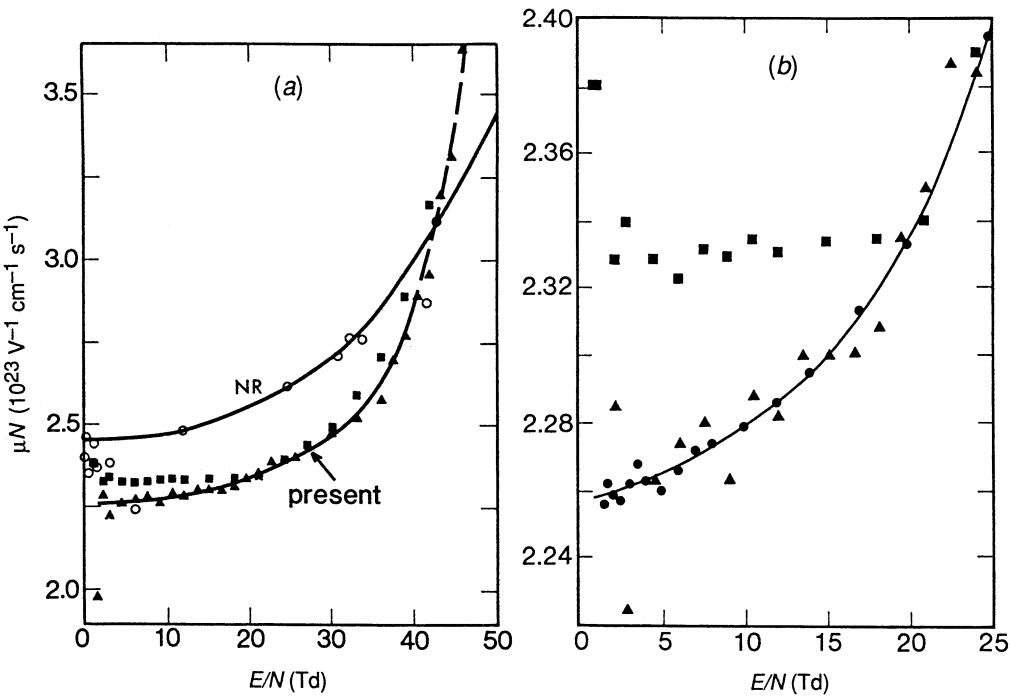

Fig. 5. (*a*) Product of the electron mobility and gas number density, μN, as a function of E/N: circles, Pack *et al.* (1962), 300 K; squares, Lowke and Rees (1963), 293 K; triangles, Wilson *et al.* (1975), 293 K assumed. The Ness and Robson (1988), 294 K, calculated, and the present results, 294 K, are shown by the curves. All of the present data points fall within the thickness of the line and have therefore not been shown. The broken curve is a smooth extrapolation of the present measurements to the data of Wilson *et al.* (1975) at values of $E/N > 40$ Td. (*b*) The low E/N range of Fig. 5*a* on an expanded scale. The solid circles and the curve give the present results at 294 K; the other symbols remain the same.

Table 2. Analysis of errors

Error	Estimated maximum effect on v_{dr} (%)	
Systematic errors		
Voltage between shutter	0·05	
Pressure	0·1	
Temperature	0·1	
Drift distance	0·1	
Extrapolation to zero open time	0·1	($E/N > 5$ Td)
	0·2	($E/N < 5$ Td)
Total systematic error	0·2	($E/N > 5$ Td)
	0·3	($E/N < 5$ Td)
Random error	0·2	($E/N > 5$ Td)
	0·3	($E/N < 5$ Td)
Total error	0·4%	($E/N > 5$ Td)
	0·6%	($E/N < 5$ Td)

4. Discussion

The present data are compared in Figs 5*a* and 5*b* with the three previous sets of values which cover the present E/N range. The drift velocity data of Wilson *et al.* (1975) required some manipulation since the drift velocities are tabled as a function of pressure p for a given value of E/p, but the temperature is not stated. In order to compare their values with the present work, the values given for different pressures at a fixed E/p value were averaged and then the data converted to μN values as a function of E/N by assuming the value of the gas temperature (293 K) which gave the best fit to the present data. It can be seen that their data (triangles) show the same monotonic decrease with E/N below 20 Td as that of the present values, whereas the earlier data of Lowke and Rees (1963) (squares) suggest that μN is approximately constant over most of this E/N region. It should be noted however that the differences between the present values and those of Lowke and and Rees for $E/N < 20$ Td lie within the combined estimated experimental errors (<±2%, Lowke and Rees; <±0·5% to 1%, present) with the exception of the values below 2 Td. The values of Pack *et al.* (1962) (circles) lie about 9% higher than the other sets of data for $E/N < 30$ Td and are subject to larger random scatter.

One significant difference between the present work and that of Lowke and Rees is that they observed a background current in all their arrival time spectra, whereas background currents were observed in the present work only at low and high values of E/N, for the reasons given in Section 3. It is probable that the background current observed by Lowke and Rees was caused by the use of low shutter signal amplitudes, but since the amplitudes they used are not known, this explanation remains a matter of speculation.

Ness and Robson (1988) have calculated values of μN for water vapour from a set of cross sections using the Boltzmann transport code of Robson and Ness (1986) and Ness and Robson (1986). Their values (upper curve in Fig. 5*a*) lie up to about 9% higher than the present values and are in agreement with the early measurements of Pack *et al.* (1962). This is expected since the momentum transfer cross section used by Ness and Robson at low energies was that derived by Pack *et al.* from their measurements of μN (thermal) as a function

of gas temperature. The present data suggest that the momentum transfer cross section drived by Pack *et al.* should be increased by approximately 9%.

5. Conclusions

The drift velocity of electrons in water vapour at 294 K has been measured over the E/N range 1·7 to 40 Td with an uncertainty which is significantly lower than that in previous measurements, thus providing more reliable data for the study of cross sections for electron scattering in water vapour at low energies. The present data confirm the finding of Wilson *et al.* that the value of μN decreases monotonically with decreasing E/N for $E/N < 20$ Td in contrast to the values of Lowke and Rees.

Acknowledgments

We wish to acknowledge the technical assistance provided by Dr T. O. Rhymes, Mr J. Gascoigne and Mr K. B. Roberts. We also wish to thank Prof. R. W. Crompton and Dr S. J. Buckman for helpful comments on this paper.

References

Elford, M. T. (1972). *In* 'Case Studies in Atomic and Collision Physics' (Eds E. W. McDaniel and M. R. C. McDowell), Vol. 2, Ch. 2 (North-Holland: Amsterdam).

Elford, M. T. (1986). Proc. 18th Int. Conf. on Phenomena in Ionised Gases (Ed. W. T. Williams), p. 130 (Hilger: Swansea).

Elford, M. T., and Robertson, A. G. (1973). *Aust. J. Phys.* **26**, 685.

England, J. P., and Elford, M. T. (1988). *Aust. J. Phys.* **41**, 701.

Gallagher, J. W., Beaty, E. C., Dutton, J., and Pitchford, L. C. (1983). *J. Phys. Chem. Ref. Data* **12**, 1, 109.

Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley–Interscience: New York).

Lowke, J. J., and Rees, J. A. (1963). *Aust. J. Phys.* **16**, 447.

Ness, K. F., and Robson, R. E. (1986). *Phys. Rev.* A **34**, 2185.

Ness, K. F., and Robson, R. E. (1988). *Phys. Rev.* A **38**, 1446.

Pack, J. L., Voshall, R. E., and Phelps, A. V. (1962). *Phys. Rev.* **127**, 2084.

Robson, R. E., and Ness, K. F. (1986). *Phys. Rev.* A **33**, 2068.

Ryzko, H. (1966). *Ark. Fys.* **32**, 1.

Wilson, J. F., Davis, F. J., Nelson, D. R., Compton, R. N., and Crawford, O. H. (1975). *J. Phys. Chem.* **62**, 4204.

Manuscript received 18 April, accepted 16 July 1990