

The Ratio D_T/μ for Electrons in Water Vapour at 294 K*

M. T. Elford

Atomic and Molecular Physics Laboratories,
Research School of Physical Sciences and Engineering,
Australian National University, Canberra, ACT 0200, Australia.

Abstract

The ratio D_T/μ for electrons in water vapour (294 K) has been measured by the Townsend–Huxley method as a function of E/N (where E is the electric field strength and N the gas number density) at vapour pressures ranging from 0.103 to 0.413 kPa. For $E/N \leq 30$ Td, where attachment and ionisation may be neglected, the values are found to be independent of vapour pressure and of the current ratio relation used to derive D_T/μ values from the measured current ratios. The uncertainty of these D_T/μ values is estimated to be $< \pm 2\%$. Values of D_T/μ measured at $E/N > 30$ Td were found to be strongly pressure dependent, the strength and sign of the dependence depending on E/N and the current ratio relation used. Since extrapolation to infinite pressure at each E/N value did not give the same value of D_T/μ , it has not been possible to derive reliable D_T/μ values for this higher E/N range. Possible causes of the observed pressure dependences are discussed. The present data are in good agreement with the values predicted by Ness and Robson for values of $E/N \leq 24$ Td.

1. Introduction

Despite the significant role played by water vapour in a wide range of discharge phenomena and the need for reliable transport coefficient data to test sets of collision cross sections (see Elford 1991), there appear to be only two previous sets of measurements of the ratio D_T/μ (D_T is the transverse diffusion coefficient and μ the electron mobility). Both these sets of data are subject to significant uncertainty. Bailey and Duncanson (1930) measured D_T/μ by a magnetic deflection method which Huxley and Crompton (1974) have indicated is subject to large errors. Crompton *et al.* (1965) used the technique devised by Huxley *et al.* (1959) for obtaining values of both D_T/μ and the difference between the attachment and ionisation coefficients. The uncertainties in this method have been discussed by Elford (1991).

Measurements of D_T/μ fall into two E/N ranges (where E is the electric field strength and N is the gas number density); from 0 to about 30 Td (1 Td = 10^{-17} V cm²) where dissociative attachment is negligible, and from about 30 Td upwards where first attachment and, at E/N values greater than about 60 Td, attachment and ionisation, are significant processes. The Townsend–Huxley diffusion chamber technique used in this work will be described in Section 2 and

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its application to the 0 to 30 Td range in Section 3. The measurements covering the higher E/N range are described in Section 4. The reliability of the relations used to derive D_T/μ from the observed current ratios is discussed in Section 5.

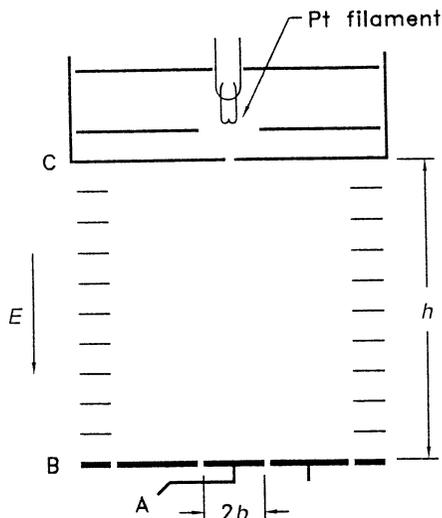


Fig. 1. Schematic of the Townsend-Huxley diffusion chamber.

2. Experimental Details

The Townsend-Huxley diffusion chamber method for measuring D_T/μ is shown schematically in Fig. 1 and described in detail by Huxley and Crompton (1974). Electrons emitted from a heated platinum filament enter the diffusion chamber through a small hole (1 mm diam.) and drift and diffuse in the vapour to a collector under the influence of a uniform electric field maintained by a series of guard electrodes at appropriate potentials. The distance h between the source electrode containing the entry hole and the collector is 100.00 mm. The collector consists of a central disk and an annulus sufficiently large in outer radius (42 mm) that the current arriving at the collector outside this radius was insignificant. The width of the gap between the disk and annulus is 0.057 mm. The ratio of the current received by the disk to that received by the annulus was measured and D_T/μ obtained from a relation based on a solution of the diffusion equation with an assumed set of boundary conditions (see later). All measurements were made at 294 K.

The water vapour used was obtained from highly pure water samples which had been carefully degassed to remove dissolved air and more particularly oxygen. Small traces of oxygen give rise to the formation of negative ions by three body associative attachment. The vapour pressures used ranged from 0.1033 to 0.4133 kPa and were measured by a capacitance manometer (MKS Baratron, Model 94AH-10SP). The maximum pressure used at a given value of E/N was determined by two conditions. The first was that the fraction of the total current falling on the disk should lie between 0.2 and 0.8 in order to avoid significant error in the measurement of the current ratio and the second was the arbitrary limitation of the potential difference across the diffusion chamber to approximately 1 kV. It may be noted that in any event it is not possible

to use water vapour pressures greater than about 1.3 kPa since the onset of large leakage currents, due presumably to the formation of water films over the insulators supporting the segments of the collector, results in large uncertainties in measurements of current ratios.

The value of E/N between the filament and source electrode (C, Fig. 1) was kept well below 30 Td for all the measurements in order to avoid the production of negative ions by dissociative attachment in this region. The only other possible source of negative ions was considered to be the hot platinum filament but tests carried out on the emission current (Elford 1991) showed no detectable negative ion component. The source current could therefore be assumed to be purely electronic.

All derivations of D_T/μ from the measured current ratios have been based on the diffusion equation. In the presence of attachment and ionisation this equation is (in Cartesian coordinates the z coordinate is in the direction of E)

$$D_T \left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) + D_L \frac{\partial^2 n}{\partial z^2} - v_{dr} \frac{\partial n}{\partial z} - v_{dr} n (\alpha_a - \alpha_i) = 0, \quad (1)$$

where $n = n(x, y, z)$ is the electron number density, D_L is the longitudinal diffusion coefficient, v_{dr} is the drift velocity and α_a and α_i are the attachment and ionisation coefficients respectively. The electron flux density $\Gamma(x, y, z)$ is given by

$$\Gamma(x, y, z) = n v_{dr} - D_L \frac{\partial n}{\partial z} \quad (2)$$

and the current ratio R by

$$R = \int_0^b \Gamma(x, y, h) 2\pi\rho \, d\rho / \int_0^\infty \Gamma(x, y, h) 2\pi\rho \, d\rho, \quad (3)$$

where $\rho^2 = x^2 + y^2$ and b is the distance between the axis and the centre of the disk-to-annulus gap. The relation obtained for R depends on the specific boundary conditions assumed (Elford *et al.* 1992).

3. Values of D_T/μ for $E/N \leq 30$ Td

In the E/N range 0 to 30 Td, α_a and α_i may be assumed to be negligible (Elford 1991). Two particular ratio relations are of interest. The first is the relation derived by Lowke (1971) who assumed that $n = 0$ at both anode and cathode and took anisotropic diffusion into account. This relation,

$$R = 1 - A(h/d'_b) \exp[-\lambda_L(d'_b - h)], \quad (4)$$

where

$$d'^2_b = h^2 + (D_L/D_T)b^2, \quad \lambda_L = v_{dr}/2D_L,$$

$$A = h/d'_b - (1/\lambda_L h) + (h/\lambda_L d'^2_b)$$

has the merit of consistent boundary conditions and moreover is in accord with the experimental fact that, in general, diffusion is anisotropic.

The second and more commonly used relation is the Huxley empirical relation (Huxley and Crompton 1974) which can be derived from the diffusion equation by assuming that diffusion is isotropic and $n = 0$ at the anode only. The cathode is assumed to behave as a geometrical plane. This relation is

$$R = 1 - (h/d)\exp[-\lambda_T(d - h)], \quad (5)$$

where $d^2 = h^2 + b^2$ and $\lambda_T = v_{dr}/2D_T$. Despite concern about the apparent non-physical nature of some of the assumptions, this relation has been found to give values of D_T/μ which are independent of pressure for a wide variety of gases, experimental geometries and range of E/N values (hence the use of the term 'empirical').

The analysis of D_T/μ data to obtain information on collision cross sections is based on the assumptions that the diffusion equation is valid (i.e. that the assumption of 'hydrodynamic' behaviour is adequate; Kumar 1984) and that the boundary conditions assumed are an accurate description of the actual behaviour of the electrons. A breakdown of either of these assumptions leads to a pressure dependence in the values of D_T/μ measured at a given value of E/N . A critical test of the validity of any set of D_T/μ data is therefore to check for such a dependence.

For small values of the ratio b/h (in the present work $b/h = 0.05$) it can be shown that, at a given value of E/N and to a good approximation,

$$(D_T/\mu)_{\text{Lowke}} = (D_T/\mu)_{\text{Huxley}}(1 - B/p), \quad (6)$$

where B is a function of $(D_T/\mu)_{\text{Huxley}}/(E/N)$ and the expression $(0.5 - D_L/D_T)$. Thus the values of D_T/μ derived using either the Lowke or Huxley relations should not be significantly different under the following conditions; at sufficiently large pressures, at sufficiently small values of $(D_T/\mu)_{\text{Huxley}}/(E/N)$ and when D_L/D_T is close to 0.5. In the case of water vapour at $E/N \leq 30$ Td, the term B/p is very much less than one, although the pressures used are relatively small. The small value of B is due to the fact that D_T/μ increases very slowly with E/N , i.e. $(D_T/\mu)_{\text{Huxley}}/(E/N)$ is small (due to the very efficient transfer of energy from electrons to water vapour molecules in inelastic collisions) and because the D_L/D_T ratio is close to 0.5.

Before commencing measurements in water vapour a series of measurements were carried out in hydrogen to check the operation of the apparatus. The values were found to agree with the values of Crompton *et al.* (1968) to within 0.5% and were independent of pressure.

The values of D_T/μ obtained for electrons in water vapour are shown in Table 1 and the average values in Fig. 2. Note that the measured values are independent of pressure. The present data extrapolate smoothly to the thermal equilibrium value of kT/e at $E/N = 0$ of 25.4 mV (where k is Boltzmann's constant, T the absolute temperature and e the electronic charge). In earlier measurements (Elford 1988) it was noted that such an extrapolation to zero E/N gave an equilibrium value which was approximately 1.5% too high. It was

Table 1. The ratio D_T/μ (in V) for electrons in water vapour (294 K)

E/N (Td)	p (kPa)			Average
	0.1035	0.137	0.288	
4.0			0.02540	0.02540
6.0			0.02570	0.02570
8.0			0.02609	0.02609
10.0		0.02610	0.02618	0.02614
12.0	0.02667	0.02627	0.02650	0.02648
14.0	0.02676	0.02655	0.02666	0.02666
16.0	0.02706	0.02687		0.02697
18.0	0.02740	0.02722		0.02731
20.0	0.02783	0.02776		0.02780
22.0	0.02834	0.02822		0.02828
24.0	0.02919	0.02889		0.02904
26.0	0.03001	0.03001		0.03001
28.0	0.03155	0.03154		0.03155
30.0	0.03439	0.03435		0.03437

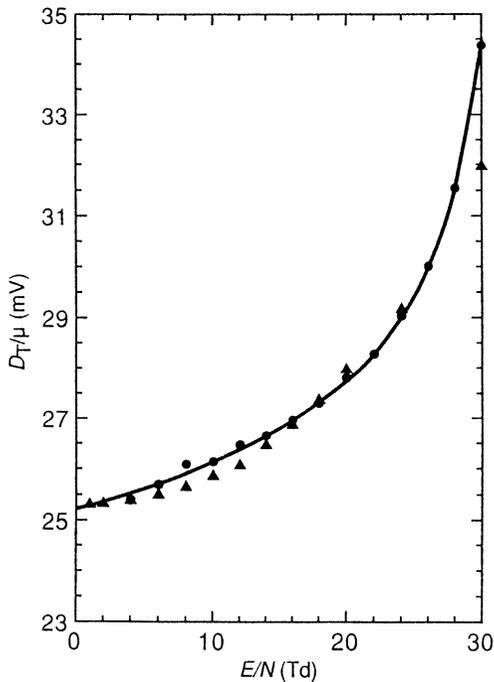


Fig. 2. Average values of D_T/μ as a function of E/N at 294 K (circles) and those calculated by Ness and Robson (1988) (triangles).

originally speculated (Elford 1988) that the error was caused by misalignment, but it was later decided that a more likely explanation was incorrect division between the disk and annulus of the collector of those electrons which arrived at the gap between these collector segments. To check this hypothesis and to ensure that this effect was not significant, the collector electrode was rebuilt with a gap of 0.057 mm between the disk and annulus, instead of 0.25 mm for

the previous collector electrode. Subsequent measurements extrapolated to the expected value. The absolute uncertainty of the D_T/μ values, for $E/N \leq 30$ Td, is estimated to be $< \pm 2\%$.

4. Values of D_T/μ for $E/N > 30$ Td

At E/N values greater than about 30 Td the current received by the collector consists of both electron and negative ion components. Since the source current in the present work is due to electrons only, it is possible to take the distribution of the negative ion current at the collector into account when deriving D_T/μ from the measured current ratio. Huxley and Crompton (1974) gave the following ratio relation based on equation (1)

$$R = 1 -$$

$$\frac{\left[\frac{h}{d'_b} - \frac{1}{\eta_h} \left(1 - \frac{h^2}{d_b^2} \right) \right] \frac{h}{d'_b} \exp[-(\eta d'_b - \lambda_L h)] - \frac{\lambda_L}{\eta} \alpha_a \int_{b'}^{\infty} \left(\int_0^h \exp(\lambda_L z) V dz \right) \rho' d\rho'}{\exp[-h(\eta - \lambda_L)] - \frac{\lambda_L}{\eta} \alpha_a \int_0^{\infty} \left(\int_0^h \exp(\lambda_L z) V dz \right) \rho' d\rho'}, \quad (7)$$

where

$$d'_b{}^2 = z^2 + (D_L/D_T)b^2, \quad \eta^2 = \lambda_L^2 + 2\lambda_L(\alpha_a - \alpha_i),$$

$$\rho'^2 = (D_L/D_T)\rho^2, \quad b'^2 = (D_L/D_T)b^2,$$

$$V = \frac{\partial}{\partial z} \left(\exp(-\eta r'/r') + \exp(-\eta r''/r'') \right),$$

$$r'^2 = \rho'^2 + z^2, \quad r''^2 = \rho'^2 + (z - 2h)^2.$$

In this relation it has been assumed that $n = 0$ at both anode and cathode and that any negative ions formed are collected at the radial distance where the attachment reaction occurred, i.e. the ions are assumed to move to the collector without diffusion. In the absence of attachment or ionisation relation (7) reverts to the Lowke relation (4).

An alternative relation for the case where ionisation and attachment occurs was obtained by Huxley (1959) and first used by Huxley *et al.* (1959) in their study of oxygen. The relation obtained was

$$R = 1 - \frac{\frac{h}{d_b} \exp[-(\eta d_b - \lambda_T h)] + \lambda_T \alpha_a \left(\frac{\eta}{\lambda_T} + \eta \right) \int_b^{\infty} \left(\int_0^h \exp(\lambda_T z) V_1 dz \right) \rho d\rho}{\exp[-h(\eta - \lambda_T)] + \lambda_T \alpha_a \left(\frac{\eta}{\lambda_T} + \eta \right) \int_b^{\infty} \left(\int_0^h \exp(\lambda_T z) V_1 dz \right) \rho d\rho}, \quad (8)$$

where

$$V_1 = \exp(-\eta r'/r') - \exp(-\eta r''/r''),$$

and where it has been assumed that $n = 0$ at the anode only, $D_L = D_T$, and that there is no diffusion of any negative ions formed. In the absence of reactions relation (8) simplifies to the Huxley empirical relation (5).

The current ratios measured (Fig. 3) are limited by the same restrictions imposed on the measurements for $E/N \leq 30$ Td. In analysing the current ratio data to obtain D_T/μ the data of Parr and Moruzzi (1972) were used for α_a/N , Ryzko (1966) for α_i/N and Wilson *et al.* (1975) for D_L/μ . The values of D_T/μ obtained using the relations (7) and (8) are shown at selected values of E/N in Fig. 4. It is apparent that both relations give values of D_T/μ which are pressure dependent and moreover they do not extrapolate to the same value at $1/p = 0$.

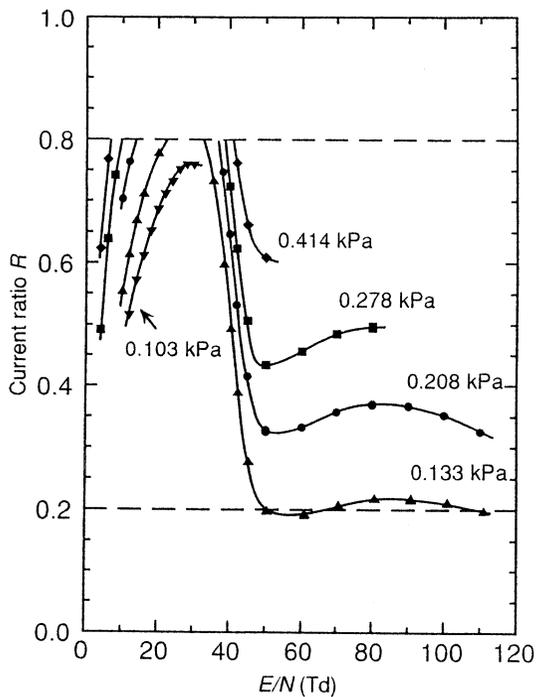


Fig. 3. Measured current ratio R as a function of E/N at the vapour pressures indicated. The dashed lines indicate the limits of 0.2 and 0.8. The apparatus parameters were $h = 100.00$ mm and $b/h = 0.05$.

5. Discussion

Ness and Robson (1988) have calculated transport coefficients for electrons in water vapour using an assumed set of collision cross sections and their multiterm transport theory. Their values (shown in Fig. 2) are in good agreement with the present data in the range 0 to 24 Td but their value at 30 Td is significantly lower.

There is no *a priori* reason why either of the sets of D_T/μ data shown in Fig. 4 for $E/N > 30$ Td should be regarded as reliable and consequently no D_T/μ values are quoted for E/N values in this range. It is of interest to speculate on the reasons for the pressure dependence in the case of water vapour.

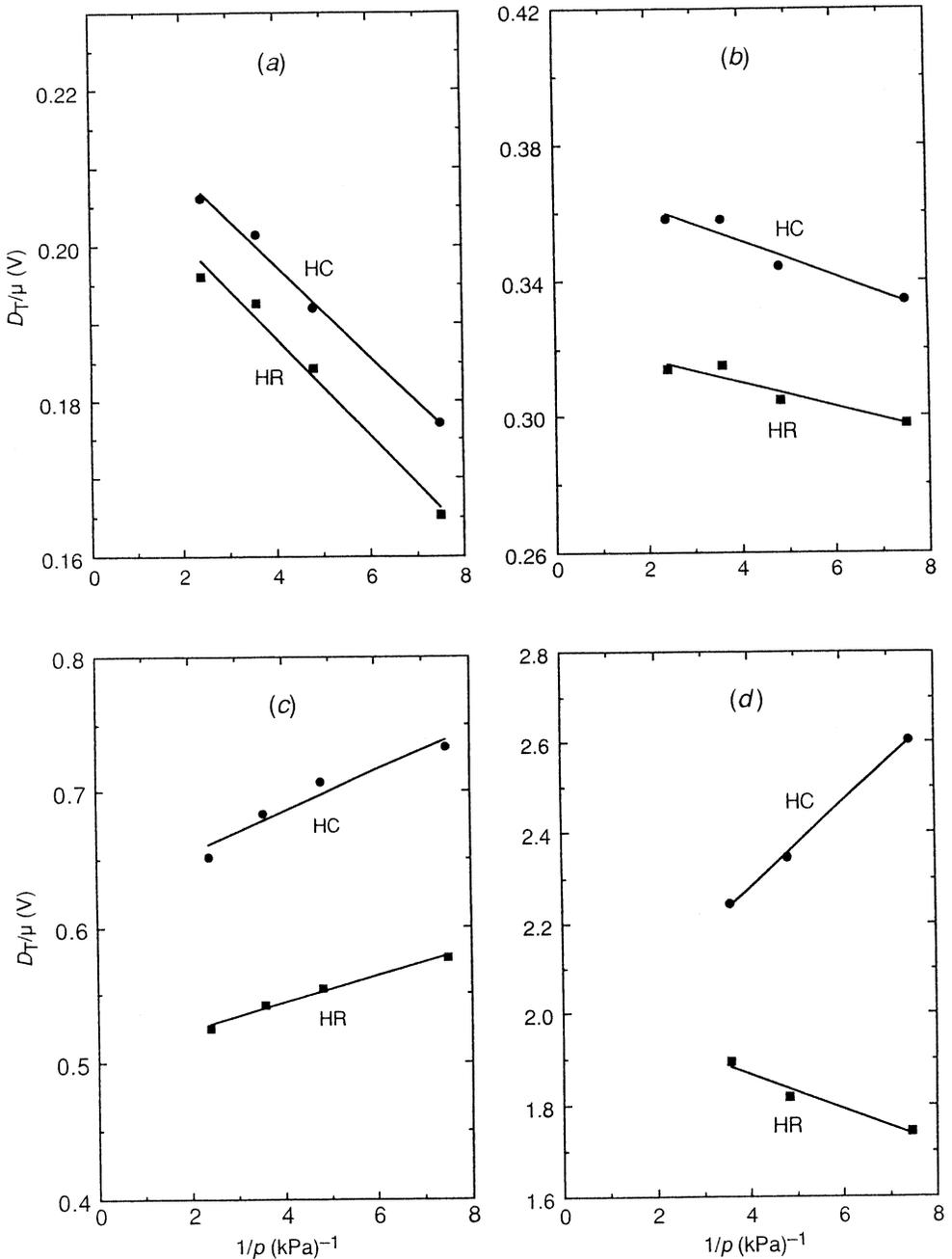


Fig. 4. Values of D_T/μ derived using relations (7) and (8) as a function of $1/p$: (a) 42 Td, (b) 45 Td, (c) 50 Td and (d) 70 Td. HC and HR denote values calculated using relations (7) and (8) respectively.

There are a number of features of these measurements which are significantly different from D_T/μ measurements in atomic and diatomic gases (Huxley and Crompton 1974) where the use of the Huxley relation has resulted in pressure independent values. The first is the restriction of the measurements to very

low pressures: in the gases referred to above, the pressures employed were about a factor of 100 times greater. The necessity of using low water vapour pressures greatly enhances boundary and non-hydrodynamic effects: if these effects are sufficiently large the diffusion equation itself would become an inadequate description of the behaviour.

The second difference is the anomalously large anisotropic diffusion which occurs at E/N values greater than 30 Td. The available D_L/μ data and rough extrapolations of calculated values (Ness and Robson 1988) suggest that the ratio D_L/D_T reaches values greater than 50 at about 55 Td. This would tend to render suspect relation (8) in which diffusion is assumed to be isotropic.

The third difference is the presence of negative ions and the assumption that the diffusion of the ions may be neglected. When the electron current components of the disk and annulus are small compared with the negative ion current components, small changes in the distribution of the negative ion current between the disk and annulus will cause a large change in the apparent electron current ratio. Hurst and Huxley (1960) showed how diffusion of the negative ions could be taken into account in relation (8) but their treatment assumed the existence of only one negative water vapour ion species. This is certainly not the case as can be seen from Fig. 5 which is a schematic of the formation and reactions of negative ions in water vapour (Elford 1991). At any given value of E/N there will be a range of negative ions that will contribute to the negative ion

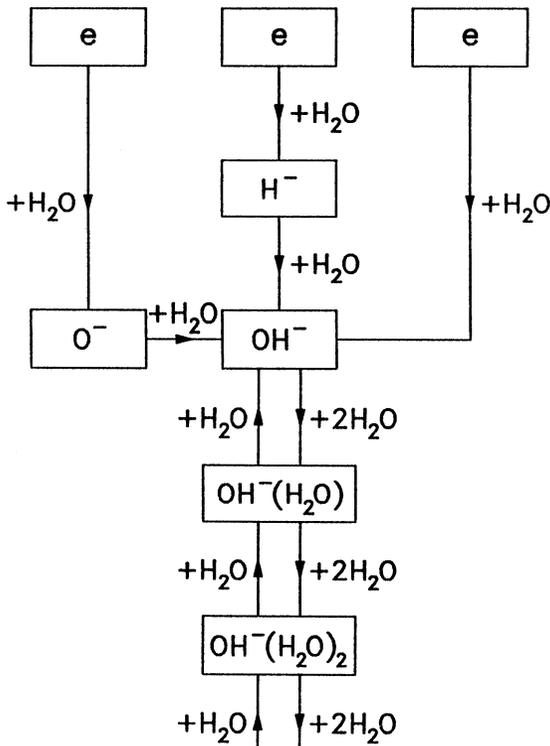


Fig. 5. Schematic of negative ion formation and reactions in water vapour.

current at the collector. Even if the theory of Hurst and Huxley were extended to cover multiple ion species, calculations of D_T/μ would require a knowledge of the relative abundances and transport coefficients of the individual negative ion species and none of this information is available.

Schmidt *et al.* (1994) have suggested that their technique for the measurement of D_T/μ could be used to obtain reliable values in the presence of attachment. By pulsing the source and using a multiple segment detector it should be possible to measure the distribution of electron current at the detector on a sufficiently small time scale that the negative ions formed in the chamber can be considered stationary. The problem of taking the contribution of the negative ion current into account at the collector can therefore be avoided. Furthermore, by measuring the variance of electron current distributions as a function of chamber length and using differencing, it should be possible to remove the effect of boundaries. Studies for such measurements are in progress (B. Schmidt, personal communication).

6. Conclusions

Although reliable values of D_T/μ have been measured for electrons in water vapour for $E/N \leq 30$ Td it would appear that the Townsend–Huxley method is not a satisfactory procedure for obtaining D_T/μ at higher values of E/N due to inadequacies in the relation which relates the measured current ratio to D_T/μ . The cause of these inadequacies is a matter of speculation. An alternative technique is required in which the measurements of electron diffusion are made independently of the presence of negative ions and where appropriate experimental corrections are made for the effects of boundaries.

Acknowledgments

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