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The Dependence of Measured Drift Velocity on Shutter Open Time in the Four Gauze Time-of-Flight Method

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Abstract

Measurements of ion transit time by the four gauze time-of-flight method have been shown previously to have a small dependence on the shutter open time. This effect has been investigated for the case of Kr^+ ions in Kr and found to be due to the combined effects of diffusion and the injection of asymmetric ion pulses into the drift space. The cause of the asymmetry and procedures for checking for the presence of an error from this source are discussed. It is estimated that the error incurred can be reduced to within the experimental scatter of the measured mobility; that is, to less than $\pm 0{\cdot}15\%$.

1. Introduction

Much of the high precision data available for ion mobilities in gases has been obtained using the four gauze time-of-flight technique (see e.g. Tyndall and Powell 1931; Beaty 1962; Beaty and Patterson 1965; Takebe *et al.* 1980; Elford 1983) in which two electrical shutters situated a known distance apart are opened and closed in synchronism.

Although there have been detailed studies of the errors inherent in the method, the dependence of the measured ion transit time t_d on the shutter open time Δt has received little attention. There appears to have been only one previous investigation, that of Kaneko *et al.* (1970), who varied the ratio $\Delta t/t_d$ from 0·07 to 0·4. They found no dependence of t_d on Δt to within the $\pm 1\%$ uncertainty of their measurements. Recently, Hegerberg *et al.* (1982) observed a small but significant dependence of t_d on Δt in measurements with Ne^+ ions in Ne and Ar^+ ions in Ar. Similar dependences have been observed for H_3^+/H_5^+ ions in H_2 (Elford 1983), Kr^+ ions in Kr (Williams and Elford 1983) and Xe^+ ions in Xe (Larsen and Elford 1986). Hegerberg *et al.* found that the measured value of t_d decreases approximately linearly as Δt increases and that by operating with small open times ($\Delta t/t_d \approx 0{\cdot}02$) the difference between the measured and extrapolated values of t_d (as $\Delta t \to 0$) could be made less than the experimental scatter of $\pm 0{\cdot}15\%$. It was assumed that the correct transit time was the extrapolated value.

In the present study, it was found that while the dependence is approximately linear for relatively large Δt, at small Δt the measured transit time decreases steeply

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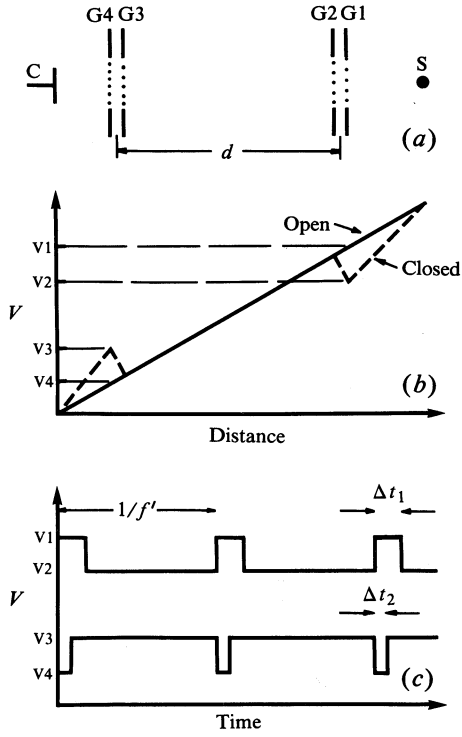

Fig. 1. (*a*) Schematic diagram of the electrode system. (*b*) The variation in potential between the collector and source. The full and dashed lines are the variations when the shutters are open and closed respectively. (*c*) The variation with time of the potentials V1 and V4 of gauzes G1 and G4 respectively.

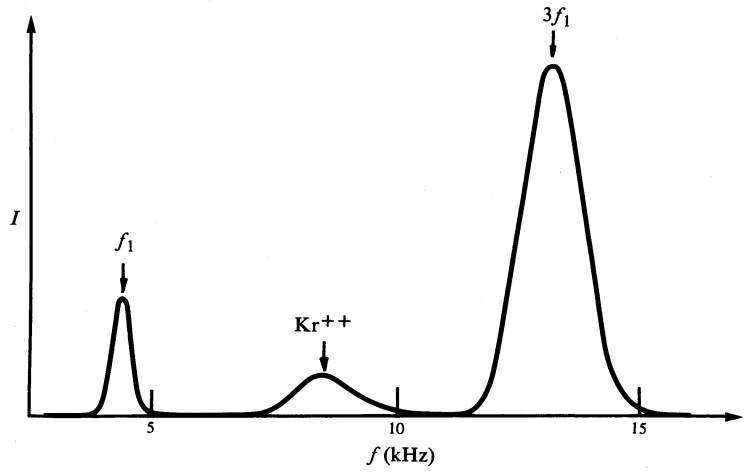

Fig. 2. Arrival time spectrum for Kr^+ in Kr showing the first and third order ion current maxima. The second order peak of the Kr^+ ion species has been removed by deleting alternate pulses applied to gauze G1 in order to show the first order current maximum of Kr^{++}. The conditions for this spectrum were as follows: $E/N = 300$ Td (1 Td $\equiv 10^{-17}$ V cm^2), $p = 11{\cdot}23$ Pa, $d = 10{\cdot}403$ cm and $\Delta t = 6$ μs.

as the open time is decreased. Thus, a linear extrapolation to zero open time is no longer justified and it is therefore important to determine how the correct transit time can be derived from the transit time measurements.

The purpose of the present investigation has been twofold; to determine the cause of the dependence of t_d on Δt, and to derive a procedure which enables the true transit time to be derived from the experimental data. The four gauze time-of-flight method is outlined in Section 2, the diagnostic procedures adopted to examine the shapes of the ion pulses transmitted by the shutter are discussed in Section 3, and the procedures adopted in an attempt to remove the effect of ion pulse shapes are described in Section 4.

2. Four Gauze Time-of-Flight Method

The measurements in the present investigation were all made using the four gauze variable-length drift tube which has been described in detail by Elford (1983). The electrode arrangement (shown schematically in Fig. 1*a*) consists of a collector C, two electrical shutters G1–G2 and G3–G4 in which the grids are high transparency (78%) metal gauzes spaced 0·5 mm apart, and a source S. The variation of potential along the electrode system (Fig. 1*b*) is maintained by a suitable system of guard rings set at appropriate potentials so that when the shutters are open there is a uniform electric field E over the length of the electrode system. The time variation of the pulses applied to the shutter grids G1 and G4 are shown in Fig. 1*c*, the pulses being in phase and derived from a master pulse train which in turn is derived from a sine wave signal of frequency f'. The time interval between pulses is equal to one period of this signal. The transmitted ion current is measured as a function of the frequency of the sine wave signal and consists of a series of current maxima at frequencies which are multiples of the first maximum [i.e. $f_1 = f_m/m$, where f_m is the frequency at which the mth maximum occurs ($m \geqslant 1$)]. The transit time t_d is given by $1/f_1$. A typical ion current spectrum is shown in Fig. 2. The alternate order peaks have been removed (by deleting alternate pulses to G1) in order to show the Kr^{++} current maximum (first order). The drift velocity v_{dr} is given by $v_{dr} = f_1\, d$, where d is the drift distance defined as the distance between the midplanes of the shutters.

The normal procedure is to operate both shutters with the same open time Δt. However, in the present investigation, the shutters have been operated with different open times; Δt_1 for shutter G1–G2 and Δt_2 for shutter G3–G4 (Fig. 1*c*). In such cases, the true transit time t_d^0 is related to the measured transit time t_d by the relation

$$t_d^0 = t_d - 0{\cdot}5(\Delta t_1 - \Delta t_2)\,. \tag{1}$$

The general continuity equation describing the time variation of the ionic number density $n(x, y, z, t)$ at all points other than the source is

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

where the electric field is in the z direction and where D_L and D_T are the longitudinal and transverse diffusion coefficients respectively. By assuming that the

radial boundaries are of infinite extent, equation (2) reduces to a one-dimensional form and has the solution (Huxley 1972)

$$n(z,\ t) = \frac{N_0'}{4\pi D_L\ t^{1/2}}\ \frac{z}{v_{dr}\ t}\ \exp\left(-\frac{(z - v_{dr}\ t)^2}{4D_L\ t}\right), \tag{3}$$

where it is assumed firstly that $n = 0$ at the source electrode (i.e. the first shutter G1–G2) except at $t = 0$, secondly that N_0' ions per unit area are transmitted and thirdly that the shutter is infinitely 'thin'.

The temporal variation of the flux Φ incident on the collector is given by (Milloy 1973)

$$\Phi = (\text{const.})t^{-3/2} \exp\{-(d - v_{dr}\ t)^2/4D_L\ t\}, \tag{4}$$

where it is assumed that the second shutter opens only momentarily. The width of the current maximum under these conditions is given by the Lowke relation (Huxley and Crompton 1974)

$$\Delta t_{1/2} = 4t_d\{(D_L \ln 2)/d\ v_{dr}\}^{\frac{1}{2}}, \tag{5}$$

where $\Delta t_{1/2}$ is the full width at half the maximum peak value. If, however, the shutters open for a finite time, which is of course the case in practice, the solution (3) requires modification.

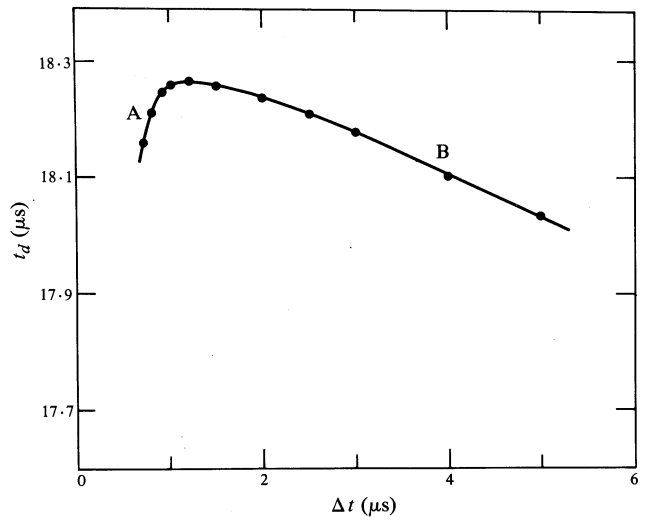

Fig. 3. Typical variation of the measured transit time t_d (as determined from the time at which the transmitted ion current has a maximum), as a function of the shutter open time Δt. The regions A and B have been termed the small and large open time effects. The conditions were $E/N = 1000$ Td, $p = 24{\cdot}7$ Pa and $d = 1{\cdot}775$ cm.

In the measurements by Hegerberg *et al.* (1982) it was found that the frequency f_1 (and hence t_d) at which the maximum ion current occurs becomes a function of the open time Δt, as is demonstrated here in Fig. 3 for the case of Kr^+ ions in Kr.

The variation with Δt depends on E/N, on the drift distance, on the E/N value in the region between S and G1, and on the gas number density. There is also a slight dependence on the pulse height. We point out that the magnitude of the overall effect is not large. For example, in Fig. 3 the measured transit time is shown to vary by 0·4% for a change in Δt from 1 to 3 μs. Nevertheless, the variation is much greater than the resolution of the measurements and therefore doubts are raised as to the correct value of the transit time and how it may be derived from such data.

3. Effect of Shutter Open Time

In order to investigate the dependence on open time, the effect has been incorporated in a theoretical description of the behaviour of the ion number density as a pulse of charge crosses the drift space.

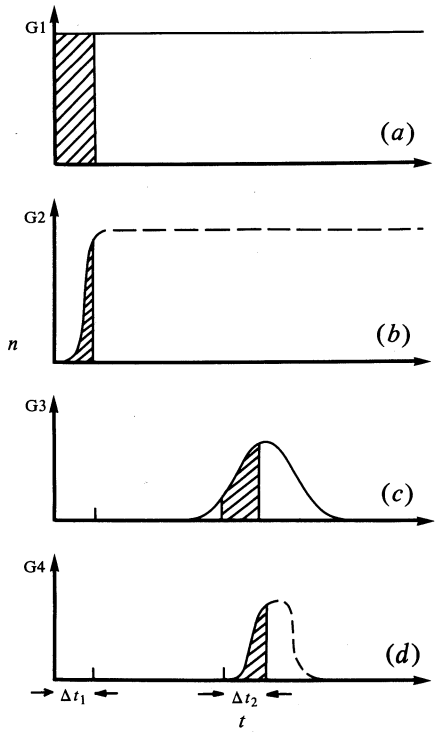

Fig. 4. Schematic diagram of the variation with time of the ion number density n at the gauzes G1 to G4 of the four gauze system. The dashed curves in (*b*) and (*d*) are the variations expected if the shutters are not closed.

The initial calculation of the transmitted ion flux to the collector for a given pulse delay time t' and shutter open times Δt_1 and Δt_2 was performed by assuming that the ion number density at gauze G1 was independent of time. The ion number density at the four gauzes of the shutter system is shown schematically in Fig. 4 as a function of time. In Fig. 4*a*, the shaded region represents those ions that are transmitted through gauze G1 during the time Δt_1 when the first shutter is open. A proportion of these ions are of course returned to G1 when the shutter closes.

The number density at the second gauze G2 was calculated using relation (3) and integrating over the open time Δt_1. The dashed line in Fig. 4*b* is the number density that would have been observed at G2 if the shutter had not closed. The ions in the

region shaded are those transmitted through G2 into the drift space. The number density at G3 (Fig. 4*c*) was calculated using relation (3) and integrating over the initial number density at G2 over time from 0 to Δt_1. If the time delay between pulses is set at t' then only those ions which arrive at G3 between t' and $t' + \Delta t_2$ will be transmitted (i.e. the region shown shaded in Fig. 4*c*). The number density at G4 (Fig. 4*d*) was calculated from (3) using the distribution shown in Fig. 4*c* as the initial number density variation. The dashed curve is the number density variation that would have been observed if the second shutter had not closed. The ions transmitted to the collector are those in the region shown shaded (i.e. in the time interval t' to $t' + \Delta t_2$) and the total flux to the collector is obtained by integrating over this transmitted pulse.

The calculation was performed with varying values of t' and fixed values of Δt_1 and Δt_2. The apparent transit time t_d was obtained by calculating the time t_d at which the flux to the collector reached a maximum value. This could then be compared with the true transit time as determined from the drift velocity and drift distance used in the calculation.

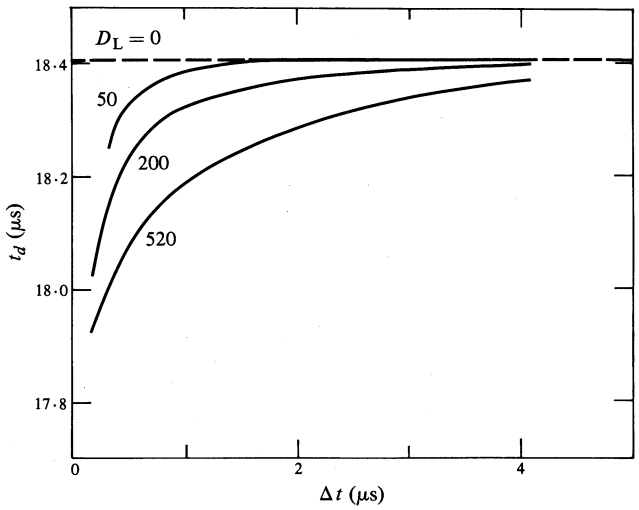

Fig. 5. Variation of t_d with Δt calculated for four values of D_L (in $cm^2 s^{-1}$) assuming the number density at G1 to be constant. The conditions assumed were $E/N = 1000$ Td, $p = 24{\cdot}7$ Pa, $d = 1{\cdot}775$ cm and a true transit time of 18·4 μs.

(a) Small Δt Effect

A typical set of calculated curves for t_d as a function of Δt and for different D_L values is shown in Fig. 5 for the case where $\Delta t = \Delta t_1 = \Delta t_2$. The decrease in t_d with decreasing Δt is evident, as shown in Fig. 3 for low values of Δt (i.e. region A). The variation arises from the change in the position of the maximum value of the number density relative to the position of the centre of mass as the pulse drifts and diffuses. Note that when there is no diffusion there is no dependence on Δt and the value of t_d calculated agrees with the true transit time. The effect, termed the 'small Δt effect', is only significant at very small values of the shutter open time. In practice, such values are usually avoided due to the low ion currents which result.

This is due to the fact that the magnitude of the ion current maximum decreases as Δt^2 when the shape of the ion current maximum is determined entirely by diffusion (i.e. at very small Δt values).

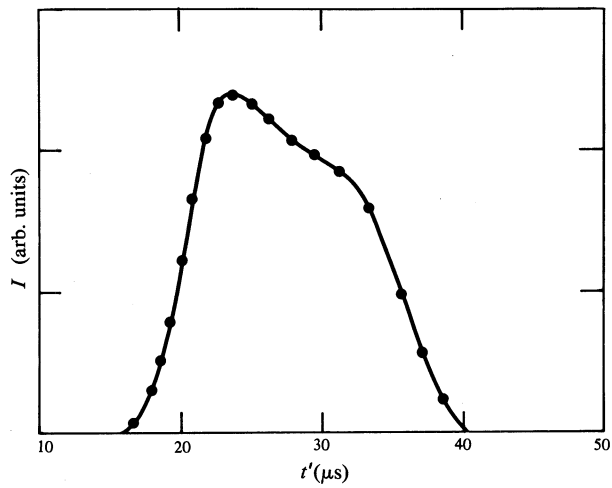

Fig. 6. Variation of ion current I with pulse delay time t' when the second shutter open time Δt_2 (0·9 μs) is very much smaller than the first shutter open time Δt_1 (16 μs). Note the current maximum at smaller delay times. The conditions were E/N = 800 Td, p = 11 Pa and d = 1·775 cm.

(b) Large Δt Effect

In considering the small Δt effect, it was assumed that the number density at G1 was constant. It was found, however, that the variation in measured transit time with Δt which was observed at large Δt values (i.e. effect B in Fig. 3) could only be simulated by assuming an appropriate arbitrary variation of the number density with time at grid G1. Such a distorted variation in n at G1 should lead to significantly distorted ion pulses in the drift tube and the possibility of distorted arrival time spectra at the collector. However, in all the early part of the experimental investigation, no evidence for asymmetry in the ion current maxima was obtained. This was subsequently found to be due to two facts. Firstly, the distortion is removed rapidly by diffusion and for significant distortion to be still present when the ion pulse reaches the second shutter, it is necessary to use very small drift lengths. Secondly, the convolution of the ion pulse distribution over the open time of the second shutter smooths out any structure in the observed current maximum. To observe such structure it was necessary to operate the second shutter at much smaller open times than the first. A measured arrival time spectrum is shown in Fig. 6, corresponding to the shortest available drift distance of 1·775 cm, and with Δt_2 set at approximately 6% of Δt_1. The peak is clearly distorted, suggesting that the number density is not constant at G1 but instead has a large maximum close to $t = 0$, as suspected from the calculations.

It does not appear possible to observe the temporal variation of number density at G1 directly, but it is possible to determine the variation at G2 by the following procedure. The open time Δt_2 is kept small and Δt_1 is varied, with the delay time

between pulses held fixed (at a value corresponding approximately to the transit time). The area of the ion current peak observed is then given by

$$A = \alpha \int_0^{\Delta t_1} n(d_0, t)\, \mathrm{d}t,$$

where α is a constant and where d_0 is the distance between S1 and S2. Thus we have

$$\mathrm{d}A/\mathrm{d}(\Delta t_1) = \alpha n(d_0, t).$$

The distribution $n(d_0, t)$ is termed the *source function.* Typical curves for A and $n(d_0, t)$ are shown in Fig. 7. The measurement of the ion current curves and the subsequent integration were performed using a standard data acquisition system based on a microcomputer, while the differentiation to obtain the source functions was performed graphically.

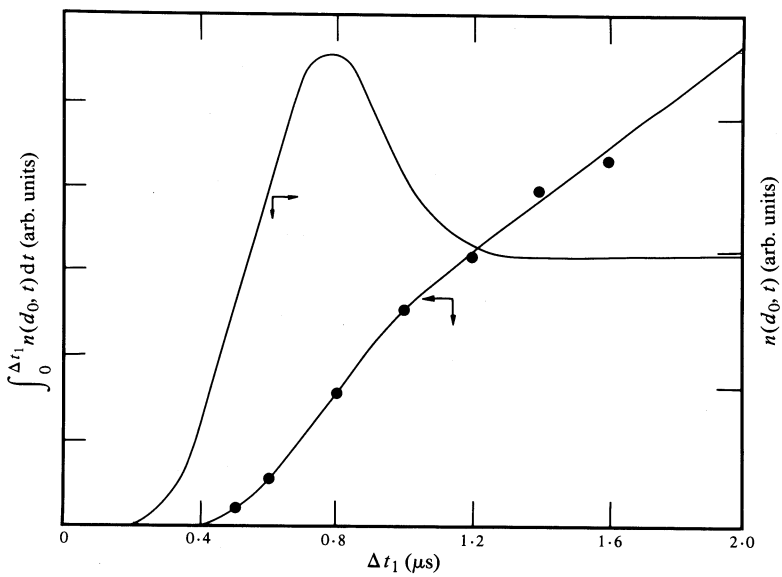

Fig. 7. Variation of the integrated pulse observed at the collector as a function of the open time Δt_1 of the first shutter (left-hand scale). The number density $n(d_0, t)$ at G2 (right-hand scale) was obtained by differentiating the first curve. The conditions were E/N = 1700 Td, p = 11·3 Pa, d = 1·775 cm and Δt_2 = 0·6 μs.

The maximum in $n(d_0, t)$ expected from the arrival time spectrum (see e.g. Fig. 6) is clearly evident in Fig. 7. We point out that the maximum expected in $n(0, t)$, that is at G1, would be expected to be significantly greater than that shown since the number density distribution at G2 has already been smoothed by diffusion.

The distribution $n(d_0, t)$ is a function of both N and E/N. The variation of $n(d_0, t)$ with E/N for a pressure of 24·65 Pa is shown in Fig. 8, normalized at large times. The disappearance of the maximum as E/N decreases may be due to the increase in the time that the ions take to travel the distance d_0 and hence in the

degree of diffusion that has occurred. There is evidence, however, from the t_d versus Δt curves and from the arrival time spectra, that even at 400 Td there is a significant maximum in the $n(d_0, t)$ function, although none was observed by the procedure described above, as is evident from Fig. 8. It would therefore appear that the maxima in the derived $n(d_0, t)$ curves are significantly underestimated. This is not surprising since at the low pressures and small gauze spacings used, boundary effects such as diffusion to the gauzes and penetration of the electric field through the gauzes may be expected to play a significant role. We note that the source functions for a given gas number density should theoretically be derivable as a function of E/N from a single source function at G1. However, attempts to obtain such a master source function were largely unsuccessful, presumably for reasons such as those given above.

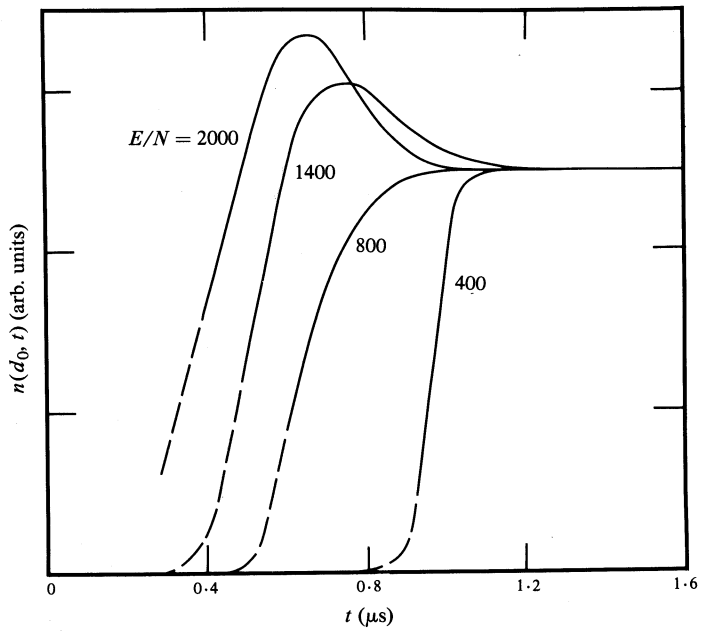

Fig. 8. Source functions $n(d_0, t)$ at grid G2 as a function of time for E/N values ranging from 400 to 2000 Td. The gas pressure was 24·65 Pa.

4. Experimental Procedures to Account for the Open Time Effect

In an attempt to eliminate the effects of asymmetric pulses, the experimental arrival time spectra were fitted using v_{dr} and D_L as adjustable parameters. The source function at G2 was first obtained from data corresponding to the smallest drift distance of 1·775 cm and by use of the procedure outlined in the previous section. Additional arrival time spectra were then taken at larger drift lengths. All the spectra were stored on disc and later fitted to obtain v_{dr}. In order to shorten the analysis, an initial estimate of D_L was obtained from the observation that the full width at half maximum $\Delta t_{1/2}$ of the ion current maximum approached a constant value at small values of Δt_1. Since Δt_2 was also small and comparable with the Δt_1 values, it was concluded that $\Delta t_{1/2}$ equalled the diffusion-limited value and that the Lowke formula

(relation 5) could therefore be used to estimate D_L. This estimate was used in the fitting procedure and it was found possible to obtain reasonable, although not perfect, fits to the data points.

It should be noted that while D_L is derived in the procedure described above, it cannot be ascribed as definitive for Kr^+ in Kr since the ion current peak is in fact the sum of two peaks, due to Kr^+ ions in the separate $^2P_{1/2}$ and $^2P_{3/2}$ spin states. The mobility of these ions differs by 3% (Helm 1975). The two separate peaks cannot be resolved using the present drift tube.

The fitted values of v_{dr} were found to be independent of Δt_1 and Δt_2 to within the experimental uncertainty of $\pm 0{\cdot}15\%$, but were not independent of the drift distance and gas pressures. Although the variations were not large (up to $\sim 1\%$) they were much larger than the resolution of the experimental measurements. The cause of these variations is not certain but is probably due mainly to the use of inadequate source functions in the calculations (see Section 3). While the calculations of arrival time spectra have enabled the qualitative features of the variation of t_d with Δt to be described satisfactorily they are not adequate when fitting is required to a precision better than 1%.

Two other approaches can be used to estimate the true transit time from the measurements. If the drift distance is more than about 5 cm, the drift velocity can be calculated from the transit time difference for two drift lengths. This procedure can largely eliminate the Δt effect. However, at very large E/N where small drift lengths must be employed in order to avoid electrical breakdown, this procedure is not satisfactory since the arrival time spectra may still be distorted by the time the pulse reaches the second shutter.

A second procedure is to gather data at open times corresponding to the position of the maximum in the t_d versus Δt curve (see e.g. Fig. 3). Although the calculated model has not been capable of predicting the exact effect in quantitative terms, it has been useful in predicting that the true transit time invariably lies above the maximum transit time, say t_d', observed in the plots. The difference between t_d' and the true transit time depends on the gas pressure and on the drift length. Thus any error from this source can be detected by measuring t_d', calculating v_{dr}, and checking that the value obtained is independent of N and d to within the experimental scatter and over the maximum possible range of N and d values. This was the procedure used by Larsen and Elford (1985) to obtain mobility data for $Xe^+(^2P_{1/2})$ and $Xe^+(^2P_{3/2})$ ions in xenon at E/N values up to 10 000 Td.

5. Discussion

The exact cause of the highly distorted variation of the number density with time at G1 is a matter of conjecture. It appears probable that the number density maximum arises from ions which are 'stored' in the potential well existing at G1 when the shutter is closed (see Fig. 1*b*). These 'stored' ions may make a number of oscillations through the gauze before being collected by the wires of the gauze.

A similar storage effect can also in principle occur at the second shutter, i.e. at gauze G3 (see Fig. 1*a*), but the ion flux to this gauze during the period when the shutter is closed is very much smaller than at gauze G1 and may be neglected.

Evidence for the explanation of ion storage is provided by varying the potential well at G1. The electric field strength in the region between S and G1 was varied by

a factor of 2 and changes in both the ion current peak shape (with small Δt_2) and the variation of t_d with Δt were observed. The effects found were consistent with the ion storage hypothesis. However, as stated above, it was not found possible to develop a simple model to explain the exact quantitative nature of the effects.

A number of previous measurements have been made with this drift tube (see Section 1) and in all cases a dependence on the open time has been observed. Fortunately, the open times used were always chosen close to that at which the maximum occurs in the t_d versus Δt curve and thus the error incurred would be expected to be small. The fact that no significant dependence on drift distance was found in these sets of data is indicative that no significant error was introduced by the effects described in this paper.

6. Conclusions

The variation of the measured ion transit times and hence drift velocities with shutter open in the four gauze time-of-flight method has been shown to be caused by the combined effects of diffusion and the presence of an anomalously high ion number density in the vicinity of the first gauze. Procedures have been developed to minimize the error involved and to check for the presence of the effect. Although the errors which arise are relatively small, it is essential that they be identified and understood in order to verify the reliability of high precision mobility data used, particularly in the derivation of cross sections.

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References

Beaty, E. C. (1962). Proc. Fifth Int. Conf. on Phenomena in Ionized Gases, Vol. 1, p. 183 (North-Holland: Amsterdam).
Beaty, E. C., and Patterson, P. L. (1965). *Phys. Rev.* **137**, A346.
Elford, M. T. (1983). *J. Chem. Phys.* **79**, 5951.
Hegerberg, R., Elford, M. T., and Skullerud, H. R. (1982). *J. Phys.* B **15**, 797.
Helm, H. (1975). *Chem. Phys. Lett.* **36**, 97.
Huxley, L. G. H. (1972). *Aust. J. Phys.* **25**, 523.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley: New York).
Kaneko, Y., Kobayashi, N., and Kanomata, I. (1970). *Mass Spectrosc.* **18**, 920.
Larsen, P. H., and Elford, M. T. (1986). *J. Phys.* B (in press).
Milloy, H. B. (1973). *Phys. Rev.* A **7**, 1182.
Takebe, M., Satoh, Y., Iinuma, K., and Seto, K. (1980). *J. Chem. Phys.* **73**, 4071.
Tyndall, A. M., and Powell, C. F. (1931). *Proc. R. Soc. London* **134**, 125.
Williams, O. M., and Elford, M. T. (1983). Proc. Third Int. Swarm Seminar, Innsbruck 1983 (Eds W. Lindinger *et al.*), p. 180.

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