Aust. J. Phys., 1987, **40**, 355–65

The Mobility of Li^+ Ions in Helium at 294 K and High E/N Values

J. P. England 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.

Abstract

The mobility of Li^+ ions in helium (294 K) has been measured at E/N values between 40 and 90 Td using the Tyndall–Powell four-gauze method. The drift distances used varied from 35 to 208 mm. Errors due to 'end effects' were taken into account by extrapolation of the mobility data to large distances. The corrected mobility values are estimated to have an uncertainty of less than 1%. The present values are compared with previous data and shown to agree to within the experimental error with values calculated from the *ab initio* interaction potential of Senff and Burton (1986).

1. Introduction

The derivation and testing of ion–atom interaction potentials by comparing predicted and measured ion transport coefficients is a well established procedure (Viehland 1983). Because of its theoretical simplicity the most extensively studied case is that of Li^+ ions in helium, and a large number of calculations of potentials and sets of ion mobility data have been published (see e.g. Cassidy and Elford 1985).

The interaction potential at large internuclear separations can now be reasonably well established due to the availability of accurate mobility data at low values of E/N (where E is the electric field strength and N the gas number density). However, to determine the repulsive part of the potential requires data of high accuracy at large E/N values. Much of the available mobility data for Li^+–He at high E/N values is subject to large statistical scatter while the values of Cassidy and Elford (1985), which have an experimental scatter of only 0·2%, do not extend beyond 70 Td. Moreover their measurements at E/N values between 30 and 70 Td were made at only one gas pressure and drift length and therefore the extent of 'end effects' could not be determined. Additional measurements to check their values for the presence of 'end effects' are therefore desirable.

The need for further high E/N mobility measurements has recently been made stronger by two developments. The first was the publication of accurate D_T/μ measurements for the Li^+–He case by Skullerud *et al.* (1986) (D_T is the lateral diffusion coefficient and μ the unreduced ion mobility v_{dr}/E, where v_{dr} is the drift velocity). These authors pointed out that their values are in significant disagreement with the values of D_T/μ calculated assuming the potential of Viehland (1983), which was based on an analysis of the mobility data of Gatland *et al.* (1977). Skullerud *et al.* suggested that the disagreement between the D_T/μ values may be due to an error in the mobility values of Gatland *et al.* and showed that an interaction potential which

0004-9506/87/030355\$02.00

gives values of D_T/μ in agreement with their experimental values predicts mobility values that are from 2 to 6% lower than those of Gatland *et al.*

The second development was a new *ab initio* calculation of the Li^+–He interaction potential by Senff and Burton (1986). This interaction potential, which has been claimed by its authors to be the most accurately calculated Li^+–He potential to date, has been used by Skullerud and Larsen (personal communication) to calculate both D_T/μ and mobility values. The agreement of the predicted and measured D_T/μ values at E/N values from 10 to 120 Td is within the stated experimental uncertainty of ±2%. The mobility values agree with those of Cassidy and Elford to within 1% up to 40 Td, but between 40 and 70 Td the difference is greater, being as much as 1·2% at 60 Td. Since the experimental error claimed by Cassidy and Elford is ±0·6% over the whole E/N range, it is clear that there is a significant discrepancy between theory and experiment.

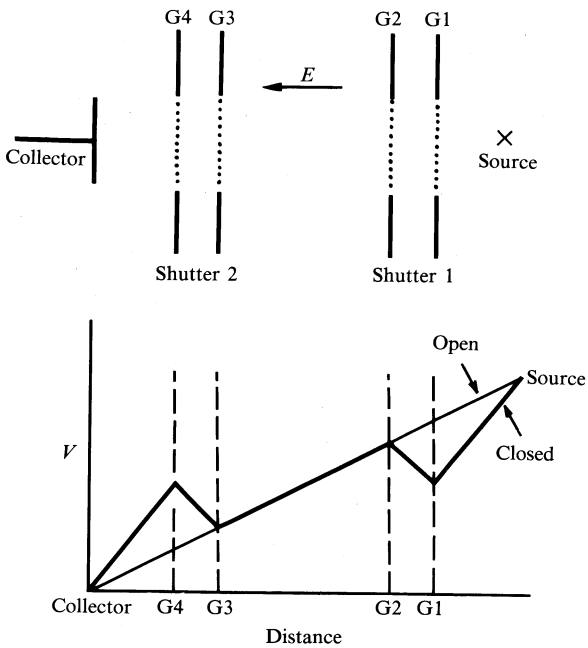

Fig. 1. Schematic diagram of the electrode system and potential distribution.

The purpose of the present work is to obtain mobility data in the high E/N range to check both the data of Gatland *et al.* and of Cassidy and Elford.

The measurements of Cassidy and Elford were made using the Bradbury–Nielsen time-of-flight method. They found this technique to become progressively less satisfactory as E/N is increased. The apparatus used in the present work and described briefly in Section 2 is of the four-gauze type which does not suffer this disadvantage.

The problems encountered in the present work are discussed in Section 2 and their significance in the interpretation of the results in Section 3. The present mobility data are then compared with other experimental data and the calculated mobility values using the Senff–Burton potential in Section 3*c*.

2. Apparatus

The variable length four-gauze drift tube used in this study has already been described in detail (Elford 1983) and only a brief description of the tube will be given here. The electrode system and potential variation are shown schematically in Fig. 1.

A uniform electric field was established within the space G2 to G3 by 'thick guard ring' electrodes (Crompton *et al.* 1965) and gauzes G2 and G3 to which potentials were applied appropriate to their position in the electrode system. The potentials applied to G1 and G4 were such as to provide reverse fields between G1 and G2 and between G3 and G4, leading to the distribution of potential down the drift tube shown in Fig. 1 (thick line). Pulses were applied at an appropriate frequency to the outer gauzes, G1 and G4, of each shutter in order to remove the potential barriers, i.e. to 'open' the shutters. The potential distribution was then as shown by the thin line, resulting in a uniform field throughout. An arrival time spectrum was obtained by measuring the current received by the collector as a function of the pulse frequency f. Each arrival time spectrum consisted of a system of peaks for each ion species present at frequencies f_n, satisfying the relation

$$f_n/n \approx v_{\mathrm{dr}}/d\,,$$

where n is an integer, d is the drift distance and v_{dr} is the drift velocity of the ion species. The relation between v_{dr} and f_n is only approximate because of 'end effects', discussed later in this section and in Section 3. The value of d in the present apparatus could be varied from $17\cdot75$ to $311\cdot13$ mm in steps of about $17\cdot8$ mm. In the measurements at high E/N, however, the drift distance was limited to about 100 mm due to the onset of electrical discharge.

The measured mobility κ_{m} is defined as

$$\kappa_{\mathrm{m}} = \frac{(f_n/n)d}{E/N}\,\frac{1}{N_{\mathrm{s}}}\,, \tag{1}$$

while the true mobility is

$$\kappa_{\mathrm{true}} = \frac{v_{\mathrm{dr}}}{E/N}\,\frac{1}{N_{\mathrm{s}}}\,,$$

which is a function of E/N and the gas temperature only. The number density is $N_{\mathrm{s}} = 2\cdot687\times10^{19}\ \mathrm{cm}^{-3}$.

Before measurements were made with Li^+ ions in helium at high E/N values the operation of the drift tube was checked by two sets of mobility measurements. The first was for He^+ ions in helium using the ion source described by Larsen and Elford (1986). The maximum difference between the values taken at 30, 100 and 200 Td and those of Helm (1977), taken with a drift tube employing Bradbury–Nielsen shutters, was $0\cdot5\%$. The second and later check was made with Li^+ ions in helium at low values of E/N, 3 and 10 Td. The measured mobilities agreed with those obtained by Cassidy and Elford (1985) to within $0\cdot1\%$.

The alkali ion source consisted of four filaments contained in an electrode structure designed to enable electric fields to be applied to deflect the ions into the drift space. Each filament produced ions by thermionic emission from a heated bead of alkali alumino-silicate glass mounted on a tungsten wire spiral filament. Temperature gradients introduced by the heat dissipated from the filament emitting Li^+ ions were found to affect the measurements reported in this paper by less than 0·1%.

The two parameters which determine the operation of the shutters are the open time and the height of the repulsive barrier. Both these parameters can affect the measured mobility.

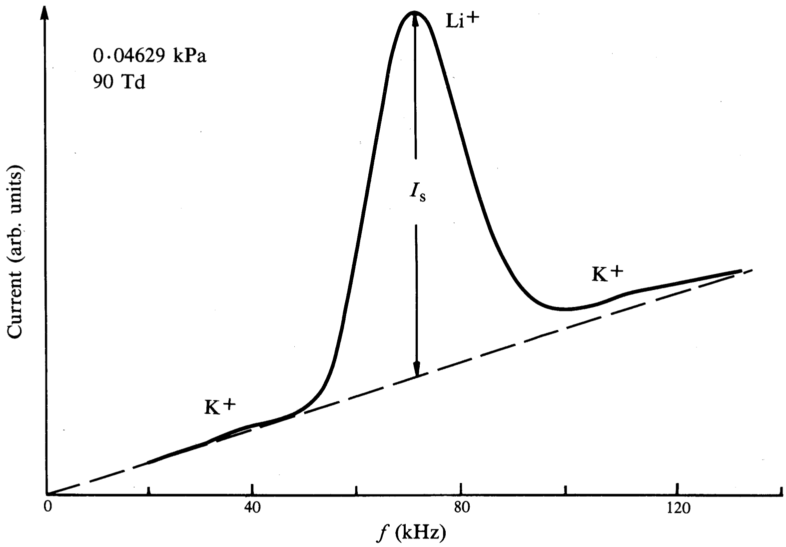

Fig. 2. Variation of the ion current received by the collector as a function of the frequency of the pulses applied to the shutter grid, i.e. an 'arrival time spectrum'. The background current shown was the largest observed in the present measurements. Alternate pulses to grid G1 were deleted electronically, thus removing the second peak (and higher even order peaks in the spectrum) and so displaying the background more clearly. Note the small current peaks due to a low abundance of K^+ ions also emitted from the coated filament. Here I_s is the signal current, i.e. the value of the current maximum above the background current.

A detailed investigation of the dependence of the measured transit time on the open time was published by Williams and Elford (1986) for Kr^+ ions in Kr. Usually the effect on mobility measurements is small and can be neglected; however, it should be noted that any significant errors from this source can be removed by determining the variation of the measured mobility with drift distance d and extrapolating to infinite d.

The dependence of the mobility on the repulsive potential barrier V_p was investigated using He^+ ions in helium at E/N values between 30 and 200 Td, pressures between 0·025 and 0·188 kPa and drift distances between 35 and 104 mm. At low values of V_p the measured mobility for a given value of E/N was independent of pressure and drift length to within the experimental scatter ($\approx$ 0·1%) indicating that no significant end effects were present. As V_p was increased to large values the measured mobility κ_m decreased and was found to be given by

$$\kappa_m = \kappa_{true}(1 - aV_p/Nd), \tag{2}$$

where κ_{true} is the true mobility and a is a constant for a given E/N value. Note that this relation holds only when this particular single end effect is present.

The reduction in κ_m with increasing pressure is thought to be due to the interpenetration of the repulsive electric field between the gauzes G1 and G2 or G3 and G4 into the drift space when the shutters are closed. This causes the electric field in the drift space near the shutters to be lowered thus increasing the ion transit time and lowering the mobility.

For most ion–atom cases the effect of field interpenetration is insignificant since only small values of V_p are required to close the shutters. However, in the case of Li^+ ions in helium at high E/N values, very large V_p values were required (e.g. 25 V) for the shutters to operate satisfactorily because of the significant proportion of the incident ions with large energies.

Even with a potential barrier of about 25 V the shutter operation was not ideal. Moreover little improvement could be obtained by increasing the barrier beyond 25 V, since the gain in shutter efficiency due to the enhanced repulsive field was offset by the increase in the ion energy in the region immediately before the shutter as a result of the increase in electric field strength and hence E/N in this region. Ions surpassing the potential barrier gave rise to a current which increased linearly with frequency. An arrival time spectrum showing such a background current is displayed in Fig. 2. The ratio R of the signal current to the total current at the position of the first current maximum decreased as the E/N value was increased, so that at 90 Td R was about 75%. As a result, measurements above 90 Td did not have the required accuracy.

It would be possible to reduce the background in the spectrum and thus increase the E/N range in a number of ways. One way would be to increase the spacing between the gauzes of the shutters in order to increase the number of collisions and hence the energy lost. This was not adopted because it required that the apparatus be reconstructed. A second would be to raise the potential of the whole electrode system before the gauze G1 by the barrier potential, so that the electric field before G1 is the same as in the drift region. This was attempted but abandoned due to electronic difficulties. A third method would be to establish a low value of E/N in the region before G1 so that the Li^+ ions have insufficient energy to surmount the potential barrier of the shutter gauzes when the shutter is shut. This method was not used since it would introduce larger end effects which could lead to additional uncertainty in the procedure used to account for them (see Section 3).

3. Results

(a) Measured Mobilities

The mobility was measured as a function of the drift distance d from 40 to 90 Td at 294 K and at pressures of 0·071 and 0·046 kPa. The results are shown in Table 1. Fig. 3 shows the values at 80 and 90 Td plotted against the inverse of the drift distance. The experimental scatter in the results is less than $\pm 0\cdot 15\%$.

(b) Corrected Mobilities

The measured mobilities are subject to a number of errors which give rise to distance and pressure dependences in the experimental results. In the present experiment, the errors which are considered to be significant arise from field interpenetration, contact

Table 1. Reduced mobility of Li^+–He at 294 K

Values are in $cm^2 s^{-1} V^{-1}$, with $V_p = 25$ V and $\Delta t = 1\cdot0$ μs

(*a*) $p = 0\cdot071$ kPa

E/*N* (Td)	*d* (mm) 35·00	52·26	69·52	86·77	104·03	121·29	138·54
40			32·30	32·33	32·40	32·40	32·43
50			32·18	32·24	32·30	32·32	
60			31·33	31·45	31·52	31·56	
70	30·29	30·51	30·57	30·67			
80	29·40	29·66	29·76				
90	28·55	28·78	29·01				

(*b*) $p = 0\cdot046$ kPa

E/*N* (Td)	*d* (mm) 35·00	52·26	69·52	86·77	104·03	121·29	138·54	155·80	173·06	207·57
40					32·61		32·62		32·61	32·62
50					32·46	32·49	32·49		32·50	
60				31·77	31·80	31·79		31·81		
70				30·93	30·94	30·95	30·98			
80		29·96	29·97	29·95	30·05	30·14				
90	29·18	29·18	29·19	29·24	29·30					

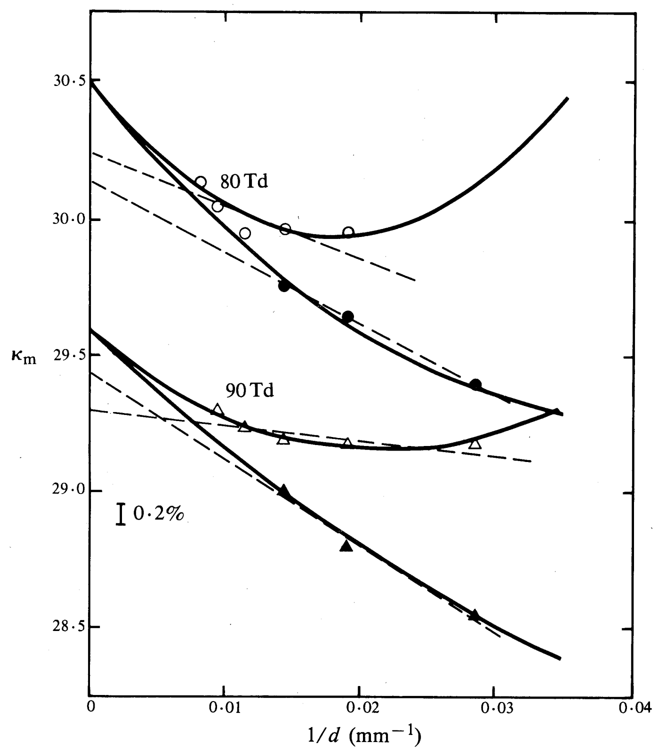

Fig. 3. Measured mobility as a function of $1/d$, where d is the drift distance, for E/N values of 80 and 90 Td and pressures of $0\cdot046$ kPa (open symbols) and $0\cdot071$ kPa (solid symbols). Dashed lines are linear fits to the data, while the solid curves are fits made using a quadratic expression in $1/d$.

potential differences, boundary effects and higher order diffusion terms. There may also be some effect due to non-hydrodynamic behaviour but the work of Skullerud *et al.* (1986) suggests that this is not significant at the E/N values and pressures used in this work. The effects are now considered in detail.

(a) Field interpenetration: This was discussed in Section 2 where it was shown that this effect gives rise to a dependence on the drift distance and number density described by relation (2).

(b) Contact potentials: Errors introduced by contact potential differences within the drift tube are inversely proportional to the potential difference across the drift space. Thus for a given E/N value the error is inversely proportional to Nd.

(c) Higher order diffusion terms and boundary effects: The variation of the ion current with time at the collector is usually analysed using a solution of the diffusion equation in which the diffusion terms appear as second order derivatives of the number density (see e.g. Milloy 1973). However, when number density gradients are large due to the presence of boundaries, extra coefficients should be included in the continuity equation (Kumar and Robson 1973). It does not seem possible to obtain the magnitude or the functional form of correction factors by solving higher order diffusion equations due to problems in stating initial number density distributions and boundary conditions.

Table 2. Comparison of the minimum potential differences for boundary effects to be negligible with the potential differences used in the measurements

E/N (Td)	ϵ_W (V)	V_{min} (V)	Potential difference (V)
40	0·74	7·4	47–94
50	1·13	11·3	59–106
60	1·55	15·5	54–109
70	2·00	20·0	42–110
80	2·48	24·8	47–110
90	2·95	29·5	35–109

The presence of significant boundary effects has been suggested by Skullerud *et al.* (1986) following computer simulations for Li^+ in helium. The computer simulations were performed for an experiment designed to measure the ratio D_T/μ and it was assumed that the collector electrode was a perfect absorber of ions and that the ions originated from a point source in the anode plane. The calculations indicated that the measured values of D_T/μ for a given value of E/N approach the true values as the parameter Nd increases. Skullerud *et al.* found that acceptable data could be obtained under conditions where the total energy eV (where $V = Ed$ and e is the ionic charge) supplied to the ions by the electric field during their transit of the drift space is greater than ten times the Wannier (1953) energy, i.e.

$$eV/c > \tfrac{1}{2}(m+M)v_{dr}^2 + \tfrac{3}{2}kT, \tag{3}$$

with $c = 10$.

The present measurements of mobilities will be affected in a similar manner by boundary effects; however, in this case, the constant c in equation (3) may be different. Values of the Wannier energy ϵ_W as a function of E/N were calculated using the present experimental mobility data and are shown in Table 2. The column $V_{\min}$ is the minimum potential difference which should be present across the drift space for boundary effects to be negligible, assuming c to have the value 10. Also shown is the range of values of V used at each value of E/N in our experiments. It can be seen that all measurements were taken using voltages that satisfied the above criterion. However, since the constant c, has not been determined for mobilities, it cannot be established whether such boundary effects have a significant effect on the present mobility measurements. Nevertheless, as with the other effects already discussed this effect becomes small as the product Nd increases.

It is the combination of the effects discussed above which is seen in the distance and gas number density dependences of the measured mobility (as defined by equation 1). Since they all occur in the same regions of the drift space, the combined effect on the ion number density distribution may produce quite complex dependences of the measured mobility on the drift distance and the gas number density. For example, diffusion effects depend on the magnitude of the electric field near the gauze, but this electric field is affected by field interpenetration. It is clear, however, that the combined effects on the measured mobility must be negligible at large drift distances. It has therefore been assumed that the measured mobility can be expanded in powers of $1/d$, i.e. that we may write

$$\kappa_{\mathrm{m}} = \kappa_{\mathrm{true}}\left(1 + \sum_{i=1}^{\infty} \alpha_i \, d^{-i}\right), \tag{4}$$

where the coefficients α_i are unknown functions of N and E/N. They may be of either sign since, while the error due to field distortion is known to reduce the measured mobility, other effects such as diffusion to boundaries increase it.

Table 3. Parameters used in the fitting procedure based on equation (4)

E/N	$p = 0{\cdot}071$ kPa		$p = 0{\cdot}046$ kPa		κ_{true}
(Td)	α_1 ($\times 10^{-3}$ m)	α_2 ($\times 10^{-5}$ m^2)	α_1 ($\times 10^{-3}$ m)	α_2 ($\times 10^{-5}$ m^2)	
40	−1·1	2·0	−0·5	4·0	32·65
50	−1·0	0·5	−1·0	7·0	32·60
60	−1·7	3·0	−1·5	8·0	32·00
70	−1·8	2·6	−1·8	9·0	31·20
80	−2·0	2·5	−2·0	6·0	30·50
90	−1·5	1·0	−1·3	3·0	29·60

Table 4. Comparison of values of κ_{true} obtained using equation (4) and either linear (LINEAR) or quadratic (QUAD) fits

E/N	κ_{true}		Difference
(Td)	LINEAR	QUAD	(%)
40	32·60	32·65	+0·15
50	32·54	32·60	+0·18
60	31·79	32·00	+0·66
70	30·93	31·20	+0·87
80	30·19	30·50	+1·03
90	29·37	29·60	+0·78

It was first assumed that only the first term in the summation in equation (4) was necessary and hence straight lines were fitted to the plots of measured mobility as a function of $1/d$ for each value of E/N and gas pressure. Fig. 3 shows some examples of the fits to the experimental data. Although the experimental scatter in the data is less than $\pm 0\cdot 15\%$, the scatter of points about the line of best fit was as much as $0\cdot 25\%$, while the values of κ_{true} found by extrapolation to infinite distance varied with pressure by up to $0\cdot 5\%$.

Both the quality of the fit and the disagreement of the extrapolated values were unacceptable and suggested that the description to first order in $1/d$ was not adequate. An analysis was therefore carried out to second order in $1/d$. Fits to the experimental data at each E/N value were obtained by requiring κ_{true} to have the same value for each pressure, but allowing α_1 and α_2 to change with pressure. In this way, all the points were fitted to within $0\cdot 15\%$. Table 3 shows the values of α_1, α_2 and κ_{true} used, and in Table 4 the values of κ_{true} obtained from the linear fit (LINEAR) and from the quadratic fit (QUAD) are shown.

Table 5. Contributions to the absolute error

	Source of error	Maximum effect on κ (%)
(a)	Systematic	
	Volume ratio	0·15
	Pressure	0·20
	Temperature	0·10
	Drift distance	0·05
	Voltage settings etc.	0·10
	Effective transit time	0·10
	Non-uniqueness of fit	0·07
	Total systematic	0·77
(b)	Random error	0·15
	Total error	0·92

Table 6. Comparison of present mobility data with the values of Cassidy and Elford and calculations by Skullerud and Larsen using the *ab initio* potential of Senff and Burton

Deviations (in %) of the experimental values from those calculated are given in parentheses

E/N (Td)	Present	Cassidy–Elford	Senff–Burton
40	32·65 (−0·3)	32·47 (−0·9)	32·75
50	32·60 (−0·3)	32·35 (−1·1)	32·71
60	32·00 (−0·3)	31·72 (−1·2)	32·11
70	31·20 (−0·5)	31·35 (−0·0)	31·36
80	30·50 (−0·3)	—	30·59
90	29·60 (−0·8)	—	29·84

The difference between the values of κ_{true} obtained from the first-order and second-order fits is 1% or less. Since the coefficients α_2 of Table 3 were one hundredth the magnitude of the α_1 values it was concluded that higher order terms in the expansion could be neglected.

The values of κ_{true} obtained from the quadratic fits were taken to be the best estimates of the mobility. The absolute error in these values was estimated to be less than $\pm 1 \cdot 0\%$ and was obtained by adding the systematic errors in quadrature and then adding the random error of $\pm 0 \cdot 15\%$ arithmetically. The contributions to the absolute error are summarised in Table 5.

(c) Comparisons with Other Data

Comparisons of experimental mobility values with the values calculated by Skullerud and Larsen (personal communication) using the Senff–Burton (1986) potential are shown in Table 6. The data of Gatland *et al.* (1977) are not given; these data are stated to be uncertain by $\pm 2\%$ below 75 Td and $\pm 4\%$ above 75 Td and have a large experimental scatter. The present data lie between 2 and 4% below the values of Gatland *et al.*, the difference increasing as E/N increases. The differences are, however, within the stated error limits.

The agreement of the data by Cassidy and Elford (1985) with the present data is within 1% and is therefore within the combined stated error limits. The agreement of the present values with the values calculated from the Senff–Burton potential is also within 1%.

4. Conclusions

The mobility of Li^+ ions in He gas at 294 K has been measured at two gas pressures, at least three different drift distances and for E/N values from 40 to 90 Td. The presence of various sources of error caused the measured mobility to be a function of the drift distance and the number density. The data were corrected by assuming a quadratic dependence on $1/d$ and extrapolation to $1/d = 0$. The error in these extrapolated values is estimated to be less than $\pm 1 \cdot 0\%$.

The experiment of Cassidy and Elford (1985) would have been subject to the same effects as found in the present investigation, except for field interpenetration which is peculiar to the four-gauze shutter system. However, since only one gas pressure and one drift length were used in their experiment for E/N values from 30 to 70 Td, these effects could not be seen and the mobility values could not be corrected to allow for them. It is believed that these errors account for the differences from the present values. The Cassidy–Elford value at 70 Td may include an additional error due to the severe background ion current problem in their experiment at this E/N value.

The present experimental mobility values agree with the values predicted by Skullerud and Larsen from the Senff–Burton interaction potential to within the experimental error. The present degree of agreement achieved by the Senff–Burton potential in predicting D_T/μ and κ values is significantly better than for any other ion–atom case studied.

Acknowledgments

The authors wish to thank Professor H. R. Skullerud and Mr P. H. Larsen for permission to use their unpublished calculations of ion mobilities and for their comments on a number of aspects of ion swarm studies. They also wish to thank Mr J. Gascoigne and Mr K. B. Roberts for technical assistance, Dr K. Kumar for discussions, and Drs R. W. Crompton and S. J. Buckman for helpful comments on this paper.

References

Cassidy, R. A., and Elford, M. T. (1985). *Aust. J. Phys.* **38**, 587.
Crompton, R. W., Elford, M. T., and Gascoigne, J. (1965). *Aust. J. Phys.* **18**, 409.
Elford, M. T. (1983). *J. Chem. Phys.* **79**, 5951.
Gatland, I. R., Morrison, W. R., Ellis, H. W., Thackston, M. G., McDaniel, E. W., Alexander, M. H., Viehland, L. A., and Mason, E. A. (1977). *J. Chem. Phys.* **66**, 5121.
Helm, H. (1977). *J. Phys.* B **10**, 3683.
Kumar, K., and Robson, R. E. (1973). *Aust. J. Phys.* **26**, 157.
Larsen, P. H., and Elford, M. T. (1986). *J. Phys.* B **19**, 449.
Milloy, H. B. (1973). *Phys. Rev.* A **7**, 1182.
Senff, U. E., and Burton, P. G. (1986). *Mol. Phys.* **58**, 637.
Skullerud, H. R., Eide, T., and Stefansson, Th. (1986). *J. Phys.* D **19**, 197.
Viehland, L. A. (1983). *Chem. Phys.* **78**, 279.
Wannier, G. H. (1953). *Bell Syst. Tech. J.* **32**, 170.
Williams, O. M., and Elford, M. T. (1986). *Aust. J. Phys.* **39**, 225.

Manuscript received 14 August 1986, accepted 13 January 1987