Transport properties of Na^+ ions in Kr gas

T. L. Tan, P. P. Ong, and M. J. Hogan
Department of Physics, Faculty of Science, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore
(Received 19 March 1993)

The transverse-diffusion coefficients for Na^+ ions drifting in Kr gas have been experimentally measured with estimated accuracies of better than 3% at E/N values ranging from 5 to 500 Td (1 Td $=10^{-21}$ V m^2) at about 303 K. In addition, elaborate calculations of the transport properties for the Na^+-Kr system have been made by using Monte Carlo simulations (MCS's) and the generalized Einstein-relation techniques. The experimental results are compared with values obtained from MCS's using the interaction potential of Koutselos, Mason, and Viehland [J. Chem. Phys. **93**, 7125 (1990)] as input. Agreement within 3% for the entire range of E/N is observed in the comparisons. MCS-calculated values of longitudinal-diffusion coefficients are also compared with those determined experimentally by Thackston *et al.* [J. Chem. Phys. **73**, 2012 (1980)].

PACS number(s): 34.20.Cf, 51.50.+v, 52.25.Fi

INTRODUCTION

Accurate experimental determination of the longitudinal- and transverse-diffusion coefficients (D_L and D_T, respectively) and mobility K of ions in a nonreacting neutral gas is of considerable importance to theoretical investigations of their mutual interaction forces [1–3]. Experimental data are often used as input in an inversion which leads to the calculation of the medium- to long-range interaction potential of the ion–neutral-atom pair. There now exists an extensive compilation of data on mobilities and longitudinal-diffusion coefficients [4–6], but little on transverse-diffusion coefficients [7–12]. The lack of data reported on D_T is basically due to some experimental limitations [2]. Because of its theoretical simplicity in analysis [13], there is a need for more experimental data on D_T.

Mobilities and values of D_L for Na^+ ions in Kr have been experimentally determined by Thackston *et al.* [14] and compiled by Ellis *et al.* [6]. This seems to be the only experimental data reported on Na^+-Kr. To our knowledge, there has hitherto been no published data on the transverse-diffusion coefficient of Na^+-Kr. Such studies of Na^+ ions in Ne and Ar have been reported [15].

In this paper, the experimental results of D_T/K, the ratio of the transverse-diffusion coefficient to mobility for Na^+ ions drifting in Kr gas at values of E/N (electric-field to neutral-gas density ratio) ranging from 5 to 500 Td (1Td $=10^{-21}$ V m^2) at 303±1 K, are presented. Results of the calculations of D_T/K and D_L/K using Monte Carlo simulations (MCS's) and the generalized Einstein-relation (GER's) techniques are also reported.

EXPERIMENTAL METHOD

The measurements were made on a newly developed drift tube which was constructed for the study of transverse diffusion of ions in neutral gas at room temperature. The apparatus has been described in detail elsewhere [16] and the procedure for analyzing the results is the same as the one used in a previous investigation [15].

Systematic checks were made to ensure the nondependence of the data on gas pressure, drift length, conditions of ion injection into the drift tube, and ion-space-charge effects. In particular, repeated measurements made at five different drift lengths for $E/N=70$, 110, and 200 Td revealed no significant change in results, thus confirming that drift-tube end effects are negligible.

In the present measurements, sodium aluminosilicates were prepared and used as the thermionic emitters of Na^+ ions, according to the method described by Hogan *et al.* [17]. In all cases, the ions present were always more than 99% Na^+. However, it should be noted that during the initial burn-in, the source produced a fairly large quantity (up to 25%) of the impurity K^+ ions. As expected, the impurity K^+ ions decayed rapidly during burn-in until only trace amounts were present. The drift chamber was always flushed and evacuated at least once with Kr gas before final introduction of the experimental gas. A residual gas analyzer, which was used to identify the neutral species present, found negligible traces of impurities, mostly residual water vapor, and Kr gas in its natural isotropic abundance. The Kr gas used in the experiments had a purity content of 99.999%.

RESULTS

Experimental values of D_T/K of Na^+ ions in Kr were obtained from the transverse-ion-current-density spectrum for E/N values from 5–500 Td. The lower limit of E/N was set by the spectrum spread which became too broad and extended into the boundary of the drift tube. The geometry of the drift tube and electrical breakdown occurring when the drift tube voltage exceeded 300 V set the upper limit of E/N to 500 Td. Results were recorded over the pressure range of 13.3–26.7 Pa at temperatures between 302 and 304 K. To facilitate comparison, all data are adjusted to a fixed temperature of 303 K using the first-order correction formula [18], given by

$$(D_T/K)[E/N, T+\Delta T]=(D_T/K)[E/N, T]+k_B\Delta T/e \ , \quad (1)$$

where the symbols are defined in Ref. [18]. The square brackets imply that the ratio D_T/K is a function of E/N and $T+\Delta T$.

Detailed experimental results are presented in Table I. Each value of D_T/K is the average of at least four independent measurements. Also given is the sample standard deviation associated with the averaged value. Judging from the magnitudes of the standard deviations in Table I, it is estimated that the random error in the values reported for D_T/K is less than $\pm 2\%$. The major contributions to the systematic error are in the pressure measurements ($\pm 0.3\%$ or less), in the knowledge of the

TABLE I. Experimentally measured values of D_T/K for Na^+ in Kr with their associated standard deviations and reduced transverse-diffusion coefficient to mobility ratios. The D_T/K values have been adjusted to 303 K.

E/N	Average D_T/K	Standard deviation		
(Td)	(mV)	(mV)	(%)	$D_T^{(r)}$
5	26.4	0.31	1.2	1.004
10	27.2	0.25	0.9	1.005
15	28.3	0.20	0.7	1.005
20	30.1	0.31	1.0	1.013
25	32.3	0.26	0.8	1.017
30	34.8	0.22	0.6	1.018
35	38.9	0.38	1.0	1.048
40	43.1	0.02	0.1	1.067
45	48.3	0.11	0.2	1.092
50	55.7	0.45	0.8	1.149
55	64.1	0.07	0.1	1.205
60	75.9	0.31	0.4	1.300
65	86.5	0.58	0.7	1.353
70	101	0.20	0.2	1.446
80	128	1.19	0.9	1.538
90	168	1.69	1.0	1.700
100	208	2.20	1.1	1.795
110	244	4.70	1.9	1.817
120	285	3.93	1.4	1.835
130	329	1.82	0.6	1.852
140	378	4.91	1.3	1.873
150	427	2.43	0.6	1.877
160	478	6.03	1.3	1.872
170	530	2.17	0.4	1.862
180	582	5.83	1.0	1.839
190	630	7.42	1.2	1.804
200	678	5.48	0.8	1.765
220	769	3.92	0.5	1.673
240	870	11.79	1.4	1.605
260	988	7.63	0.8	1.565
280	1095	12.00	1.1	1.504
300	1229	8.09	0.7	1.478
340	1500	8.28	0.6	1.413
380	1741	21.15	1.2	1.320
420	2054	11.37	0.6	1.279
460	2277	20.41	0.9	1.185
500	2551	32.84	1.3	1.126

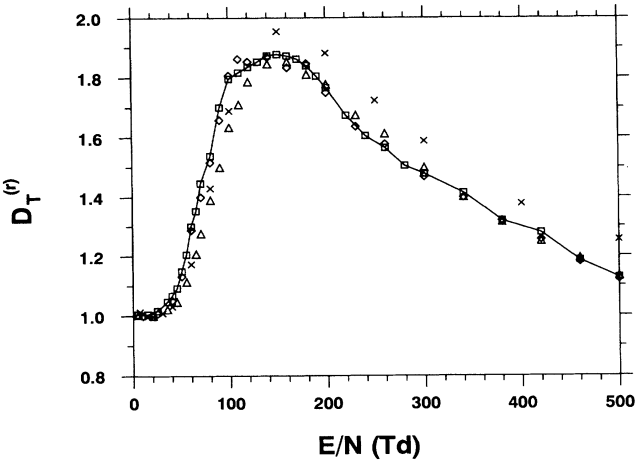

FIG. 1. Reduced transverse-diffusion coefficient to mobility ratios of Na^+ in Kr plotted against E/N. Squares (connected by straight lines) and diamonds represent the present experimental data and MCS-calculated values using the KMV potential, respectively. Triangles and crosses represent GER-calculated values using mobilities from MCS calculations and from Thackston *et al.* [14] respectively.

TABLE II. MCS calculated values of K_0, D_T/K, $D_T^{(r)}$, D_L/K, and $D_L^{(r)}$ using the KMV potential.

E/N	T_{eff}	K_0	D_T/K		D_L/K	
(Td)	(K)	($cm^2\ V^{-1}\ s^{-1}$)	(mV)	$D_T^{(r)}$	(mV)	$D_L^{(r)}$
5	306	2.22	26.9	1.021	26.2	0.995
10	315	2.23	27.0	0.999	27.4	1.013
15	330	2.24	27.8	0.988	28.6	1.016
20	352	2.24	29.5	0.993	30.2	1.017
25	379	2.24	32.0	1.008	35.6	1.121
30	413	2.25	35.1	1.026	39.3	1.149
35	460	2.30	38.4	1.036	46.0	1.240
40	511	2.32	42.5	1.051	54.6	1.349
45	571	2.34	48.1	1.086	65.6	1.483
50	648	2.39	54.9	1.131	81.0	1.669
55	738	2.44	64.2	1.206	101	1.895
60	842	2.49	75.2	1.288	119	2.044
65	969	2.55	86.5	1.353	144	2.245
70	1 125	2.63	98.1	1.400	170	2.431
80	1 460	2.73	127	1.516	223	2.675
90	1 865	2.82	164	1.658	271	2.740
100	2 371	2.92	209	1.806	305	2.632
110	2 891	2.97	251	1.862	350	2.603
120	3 488	3.02	287	1.852	381	2.455
140	4 696	3.04	377	1.868	445	2.205
160	6 003	3.03	469	1.833	513	2.009
180	7 281	2.98	584	1.846	590	1.863
200	8 745	2.95	673	1.749	645	1.676
230	10 767	2.86	818	1.635	779	1.557
260	13 156	2.80	997	1.577	902	1.427
300	16 215	2.70	1222	1.467	1068	1.282
340	19 401	2.61	1485	1.398	1313	1.236
380	22 719	2.53	1741	1.319	1490	1.128
420	26 297	2.47	2017	1.255	1728	1.075
460	30 108	2.41	2270	1.180	1931	1.004
500	33 786	2.35	2540	1.120	2220	0.979

drift length (±0.3% or less), and in the approximations (±0.3% or less) made in deriving the equation for the ion-current-density spectrum. The total error for the experimental data is estimated to be ±3%.

Ratios of the transverse- or longitudinal-diffusion coefficient to mobility (D_T/K or D_L/K, respectively) can be presented effectively [12] in a reduced form given by

$$D_{T,L}^{(r)} = (e/k_B T_{\text{pol}})(D_{T,L}/K) , \quad (2)$$

where

$$T_{\text{pol}} = T + M(N_0 K_{\text{pol}} E/N)^2/3k_B . \quad (3)$$

This reduced form removes both the $(E/N)^2$ and the first-order temperature dependence of $D_{T,L}/K$ and amplifies the details of the variation of the diffusion coefficients with E/N.

Figure 1 shows a plot of $D_T^{(r)}$ with E/N for Na^+ ions in Kr.

The Koutselos-Mason-Viehland (KMV) interaction potential [19] of the Na^+-Kr system, which is the only reliable one available, is used as input in our high-speed MCS calculations. Details of the method have been previously reported [8,12,20] and results are shown in Table II. Confidence in the broad applicability of the KMV potential for the alkali-metal-ion-rare-gas interaction has been built up from several previous investigations involving different interaction pairs [8–12]. Values of T_{eff}, K_0, D_T/K, $D_T^{(r)}$, D_L/K, and $D_L^{(r)}$ are presented. Repeated calculations covering 2.5 million collisions show that the reproducibility of the results is better than 1% for mobility and 2.5% for $D_{T,L}$. These results are shown graphically in Figs. 1 and 2, as plots of $D_T^{(r)}$ and $D_L^{(r)}$, respectively.

To our knowledge, the only experimentally determined values of K_0 and ND_L for Na^+ in Kr are those due to Thackston *et al.* [14]. These results were later compiled by Ellis *et al.* [6] and derived quantities of T_{eff} were determined. Unfortunately, we have found that both the derived values of T_{eff} and the numerical values of ND_L given by Ellis *et al.* were inconsistent with the original data of Thackston *et al.* Consequently, we decided to calculate the quantities of T_{eff} and D_L/K based on the original data of Thackston *et al.* Values of D_L/K and $D_L^{(r)}$ are given in Table III and plotted in Fig. 2.

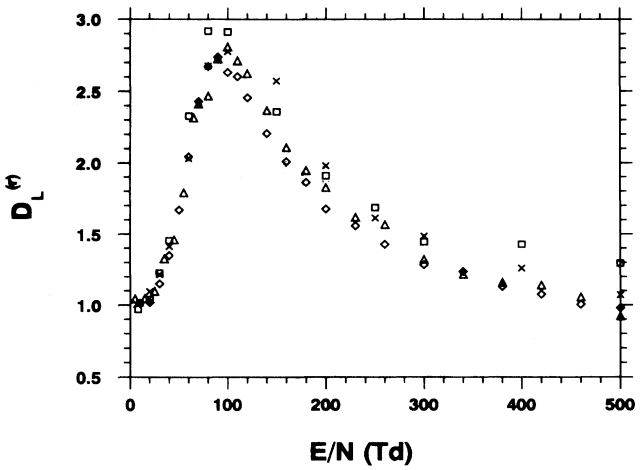

FIG. 2. Reduced longitudinal-diffusion coefficient to mobility ratios of Na^+ in Kr plotted against E/N. Squares and diamonds represent the experimental data of Thackston *et al.* [14] and MCS-calculated values using the KMV potential, respectively. Triangles and crosses represent GER-calculated values using mobilities from MCS calculations and from Thackston *et al.* [14], respectively.

We have also used Waldman and Mason's parametrized version [21] of the generalized Einstein relations to compute D_T/K and D_L/K values from both the mobility data of the MCS calculations and those of Thackston *et al.* [14]. Results are given in Table IV and plots of $D_T^{(r)}$ and $D_L^{(r)}$ are included in Figs. 1 and 2, respectively.

TABLE III. Derived values of v_d, T_{eff}, D_L/K, and $D_L^{(r)}$ from the experimental mobilities K_0 and longitudinal-diffusion coefficients ND_L of Thackston *et al.* [14].

E/N (Td)	ND_L (10^{-18} cm^{-1} s^{-1})	K_0 (cm^2 V^{-1} s^{-1})	v_d (cm s^{-1})	T_{eff} (K)	D_L/K (mV)	$D_L^{(r)}$
7	1.53	2.20	4 138	309	25.9	0.975
8	1.53	2.20	4 729	311	25.9	0.970
10	1.58	2.20	5 911	315	26.7	0.990
15	1.68	2.20	8 867	329	28.4	1.010
20	1.83	2.21	11 877	350	30.8	1.038
30	2.54	2.26	18 218	414	41.8	1.224
40	3.65	2.31	24 828	510	58.8	1.454
60	9.20	2.52	40 627	857	136	2.327
80	18.2	2.78	59 759	1 503	244	2.919
100	27.0	2.98	80 073	2 457	337	2.913
150	45.0	3.12	125 752	5 615	537	2.357
200	60.0	3.04	163 370	9 268	735	1.910
250	77.0	2.90	194 808	13 050	988	1.685
300	89.9	2.78	224 096	17 172	1 204	1.445
400	145	2.59	278 373	26 332	2 084	1.427
500	193	2.45	329 158	36 696	2 932	1.293

DISCUSSION

Figure 1 shows that the present experimental data of $D_T^{(r)}$ agree so well with those of the MCS calculations using the KMV interaction potential that the latter may also be represented by almost the same curve. The only slight difference is that the experimental values give a smoother curve around the peak region from $E/N = 110-170$ Td, which thus yields a more accurate value of the peak position of the $D_T^{(r)}$ plot. The values calculated from the GER using the MCS-derived mobility values as input agree very well with both experimental and the directly calculated MCS values at E/N above 200 Td and at very low E/N. However, these GER values are 4–11 % below them for intermediate E/N values between 40 and 120 Td. GER calculations are not expected to be accurate when the ion–neutral-atom mass ratio is not negligible and in the E/N region where the mobility rises rapidly. This inaccuracy of the GER is similar to that found in the three-temperature theory [2] from which the GER formulas were derived. At moderate and high values of E/N, there is a significant difference between the GER-calculated values derived from the mobility data of Thackston *et al.* [14] and the rest of the $D_T^{(r)}$ data. This discrepancy is probably due to a systematic error in the mobility measurements made with the Georgia Tech drift-tube mass spectrometer. Such trends were similarly observed for Na^+ ions in Ar and Ne [15] and others [7,22]. A brief discussion concerning the discrepancy is presented by Hogan and Ong [15].

A comparison of the various $D_L^{(r)}$ data is shown in Fig.

TABLE IV. GER calculated values of D_T/K, $D_T^{(r)}$, D_L/K, and $D_L^{(r)}$ using the MCS mobility values, and the experimental mobility data of Thackston *et al.* [14].

	Based on MCS mobility values				Based on experimental mobility values [14]			
E/N (Td)	D_T/K (mV)	$D_T^{(r)}$	D_L/K (mV)	$D_L^{(r)}$	D_T/K (mV)	$D_T^{(r)}$	D_L/K (mV)	$D_L^{(r)}$
5	26.4	1.002	27.5	1.044				
7					26.9	1.013	26.7	1.005
8					26.7	1.000	26.9	1.008
10	27.0	0.999	27.7	1.025	27.0	0.999	27.4	1.014
15	28.1	0.999	29.4	1.045	28.1	0.999	29.3	1.041
20	29.7	1.000	31.5	1.061	29.6	0.997	32.5	1.094
25	31.8	1.003	34.8	1.097				
30	34.4	1.006	41.8	1.223	34.5	1.009	41.5	1.214
35	37.9	1.022	49.1	1.324				
40	41.7	1.031	53.2	1.315	41.7	1.031	57.1	1.412
45	46.3	1.046	64.6	1.460				
50	52.2	1.076	80.8	1.666				
55	59.2	1.113	95.3	1.791				
60	67.2	1.152	116	1.988	68.4	1.172	119	2.032
65	77.2	1.207	148	2.314				
70	89.4	1.277	169	2.414				
80	116	1.390	206	2.469	119	1.429	223	2.678
90	148	1.500	269	2.727				
100	189	1.634	325	2.810	195	1.689	321	2.778
110	230	1.710	365	2.714				
120	277	1.786	407	2.625				
140	372	1.845	477	2.366				
150					445	1.954	585	2.572
160	473	1.852	538	2.107				
180	572	1.809	615	1.945				
200	683	1.778	702	1.827	723	1.881	761	1.979
230	836	1.673	808	1.617				
250					1009	1.722	945	1.613
260	1018	1.612	989	1.566				
300	1246	1.498	1098	1.320	1320	1.587	1235	1.484
340	1485	1.399	1289	1.215				
380	1735	1.315	1528	1.158				
400					2008	1.377	1835	1.258
420	2006	1.249	1830	1.140				
460	2290	1.192	2028	1.056				
500	2562	1.131	2085	0.921	2841	1.254	2425	1.071

2. The directly calculated MCS data for $D_L^{(r)}$ agree fairly well with those calculated from MCS mobility data using the GER relations. The experimental data of Thackston *et al.* [14] and the GER calculations using their mobility data were found to be higher than the MCS-derived data at moderate and high values of E/N. Relatively close agreement exists for all data below the peak region of about $E/N=100$ Td.

Further evidence of the accuracy of the MCS calculations may be obtained from a plot of D_T/K and D_L/K with $(E/N)^2$. Theoretically as E/N tends to zero, D_T/K and D_L/K should merge and vary linearly. This behavior is shown in Fig. 3, and both D_T/K and D_L/K approach the theoretical limit of 26.1 mV for $T=303$ K as $E/N\rightarrow 0$ as predicted by the Einstein equation,

$$D_{T,L}/K=k_BT/e\ . \tag{4}$$

Our experimental values of D_T/K are included in the plots for comparison.

It can be seen from Figs. 1 and 2 that the transverse-diffusion peaks at around $E/N=150$ Td, in contrast to the peak at about 90 Td for the longitudinal diffusion. This apparent shift in the peak can be explained in terms of an additional collision energy attributed to the forward ion drift velocity in the longitudinal-diffusion coefficient. This shift is similarly observed for the Li^+-He system [20]. The MCS calculations are expected to be more jagged since they are strictly based on random numbers and no correlation exists between calculations of (even) neighborhood E/N points. However, the jaggedness is always maintained within the errors of the calculations, which are only a function of the statistical size of the samples used as input. On the other hand, the experimental data are inherently smoother, as expected, since errors in all experimental input parameters permeate smoothly across different E/N settings.

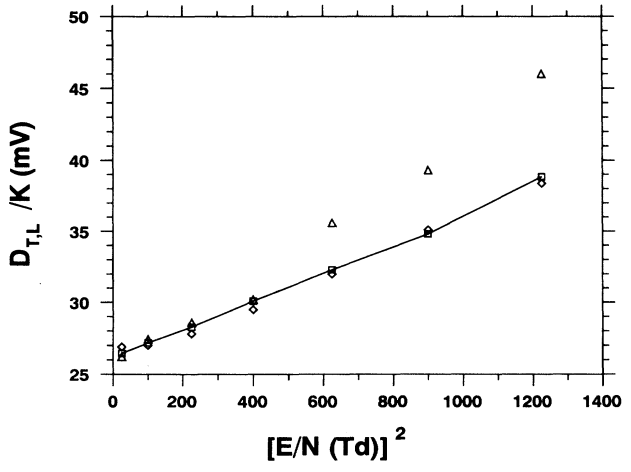

FIG. 3. Plots against $(E/N)^2$ of the MCS-calculated D_T/K (diamonds) and D_L/K (triangles) using the KMV potential and present experimental D_T/K (squares connected by straight lines), showing their expected zero-field limit of 26.1 mV at 303 K.

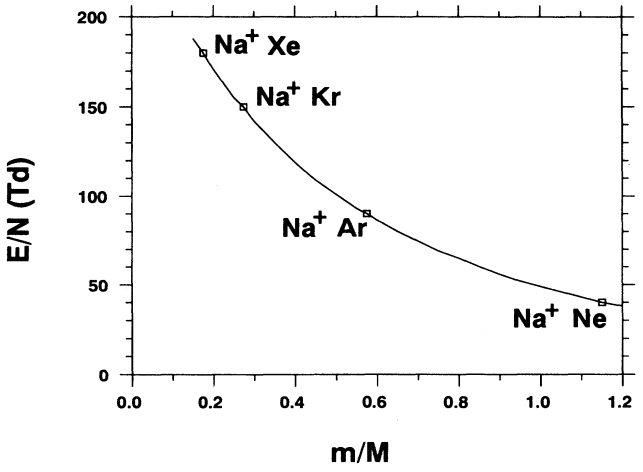

FIG. 4. Plots against the ion-to-neutral-atom mass ratio (m/M), of E/N at which the maximum $D_T^{(r)}$ occurs, for various Na^+–noble-gas systems.

The Na^+-Ne and Na^+-Ar [15], and the Na^+-Kr systems appear to indicate a relationship between m/M (ion-to-neutral-atom mass ratio) and the value of E/N corresponding to the maximum value of $D_T^{(r)}$ for the alkali-metal-ion–noble-gas system. For Na^+-Ne, Na^+-Ar, and Na^+-Kr, the values of m/M are 1.15, 0.575, and 0.274, respectively. The maximum values of $D_T^{(r)}$ occur at $E/N=40$, 90, and 150 Td, respectively. From a recent preliminary experimental study of Na^+ ions in Xe gas [23], a plot of $D_T^{(r)}$ gives a maximum value at 180 Td. The m/M value of Na^+-Xe is 0.175. A relatively smooth trend of m/M with E/N corresponding to the maximum value of $D_T^{(r)}$ is shown in Fig. 4. Attempts to obtain a more general correlation between the peaks of transport coefficients and the values of E/N at which the peaks occur for different m/M ratios are in progress.

CONCLUSION

We have presented experimental data of D_T/K for the heretofore unstudied system of Na^+ ions in Kr with an overall accuracy of 3% in the range $E/N=5$–500 Td. They provide values which may be used as input data for the determination of ion–neutral-atom interaction potential particularly in the medium- and long-range regions, and with which theoretical calculations can be compared. Our MCS calculated values of D_T/K and D_L/K have reaffirmed the validity of the KMV potential curve for the Na^+-Kr system. Experimental values of D_T/K were found to be in excellent agreement with the calculations of the MCS method based on the KMV potential. The present experimental data would hopefully contribute to the scarce pool of transverse diffusion coefficient data from which a general functional form of its peak value at a certain value of E/N for different ion–neutral-atom mass ratios can hopefully be established.

ACKNOWLEDGMENTS

We would like to acknowledge the able technical assistance of Mr. Wu Tong Meng. This work was supported by National University of Singapore Grant No. RP910651. We are also indebted to staff of the University's Computer Centre for professional advice on the optimal use of the university's supercomputer.

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