Mobility of He^+, Ne^+, Ar^+, N_2^+, O_2^+, and CO_2^+ in their parent gas

E. Basurto,* J. de Urquijo,† I. Alvarez, and C. Cisneros
Centro de Ciencias Fisicas, P.O. Box 48-3, 62251 Cuernavaca, Morelos, Mexico
(Received 17 September 1999)

We have used a drift tube with double mass spectrometry to measure the mobility of He^+, Ne^+, Ar^+, N_2^+, O_2^+, and CO_2^+ in their parent gas over a wide range of the density-normalized electric field, E/N, from 70 to $12\,500\times10^{-21}$ V m^2. In all cases, the E/N ranges have exceeded those hitherto found in the literature, especially those of Ar^+ in Ar and N_2^+ in N_2. Our mobility data are in fair to excellent agreement with previous experimental data in the overlap range. Recent calculated data for the mobility of Ar^+ in Ar show excellent agreement with our data at high E/N, while fair agreement was observed for the calculated data of the systems N_2^+ in N_2 and O_2^+ in O_2. Also, the Ar^+ in Ar mobilities for $E/N>10$ kTd were found in excellent agreement with those derived from the measurement of the mean ion energy in diffuse Townsend discharges (1 Td=1 townsend=10^{-21} V m^2). To the best of our knowledge, over some E/N ranges, our data were found to be the first to be reported.

PACS number(s): 52.20.Hv, 52.25.Fi, 34.70.+e, 51.50.+v

I. INTRODUCTION

When an ion drifts in its parent gas, resonant charge transfer is the predominant process, its respective cross section bearing a direct relation with its mobility, which is usually measured by swarm techniques over an energy range that may extend up to a few tens of eV [1–2]. Compilations [3] of the mass-analyzed mobility of ions in parent gas indicate that these have been concentrated mostly on the lower region of the density-normalized electric field intensity ratio E/N where only a few cases are found covering the intermediate and high-field regions. Recently, diffuse discharges in a Townsend experiment have been used to study transport phenomena and reactions of ions in parent gases, mostly focused to the obtention of resonant charge transfer cross sections and ion energy distributions [4].

The relay mechanism taking place during resonant charge transfer is a very efficient process for fast neutral production, which can, for instance, explain important phenomena on secondary electron production in nitrogen discharges at very high E/N due to neutral impact upon cathode surfaces [5].

With only a few exceptions, drift tube techniques applied to the measurement of ion mobility have been concentrated mostly at the lower E/N range, up to a few hundred Townsend (1 Td=10^{-21} V m^2). There is an increasing need of transport data for the modeling and simulation of gas discharges, many of them in the high-E/N regions. Thus we have used a recently modified drift tube technique to allow mobility measurements up to values exceeding 10 kTd, such as the case of Ar^+ in Ar.

Herein, we report of an improved drift tube technique to measure the mobility of He^+, Ne^+, Ar^+, N_2^+, O_2^+, and CO_2^+ in their parent gases over a wide range of E/N, from 0.07 to 12.5 kTd.

II. EXPERIMENT

The drift tube with double mass spectrometry (DTDMS) used for this research is an improved version of the drift tube-mass spectrometer that was described thoroughly in Ref. [6]. The ion source of this apparatus was modified substantially by inserting a quadrupole mass spectrometer to its exit end. A schematic of the modified mass-analyzed ion source is shown in Fig. 1. Primary ions, produced by electron impact in the hot-filament source, are focused by an array of four cylindrical, electrostatic lenses into the entrance of the quadrupole mass spectrometer (QMS) with a mass range of 150 amu, and mass resolution of 0.1 amu. The ion source chamber can be moved over a distance from 0 to 38.70 $\pm$0.05 cm at 13 discrete positions, defined by a set of 3.1 cm-wide guard rings.

After mass analysis, the ions are focused by a second set of electrostatic lenses through an orifice of 0.2 mm into the drift space. Upon entrance into this region, the ions may have an excess translational energy of up to about 20 eV, which is relaxed over the first 3.1 cm of drift space, by collisions with the neutrals, subjected to the same E/N conditions as those prevailing in the drift region. In particular, this process is very efficient for the resonant systems herein con-

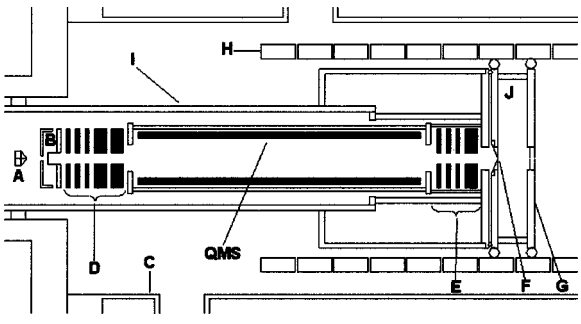

FIG. 1. Schematic of the modified ion source of the drift tube. *A*, gas feed; *B*, ionizing region; *C*, main drift chamber; *D*, entrance ion optics; *E*, exit ion optics; *F*, skimmer; *G*, ion shutter plate; *H*, guard rings; *I*, ion source vacuum chamber; QMS, quadrupole mass spectrometer; *J*, ion relaxation region.

*Also at ESFM, IPN, Edif. 9, UP-ALM, C.P. 07738, México, DF, Mexico
†Author to whom correspondence should be addressed. Electronic address: jdu@ce.fis.unam.mx

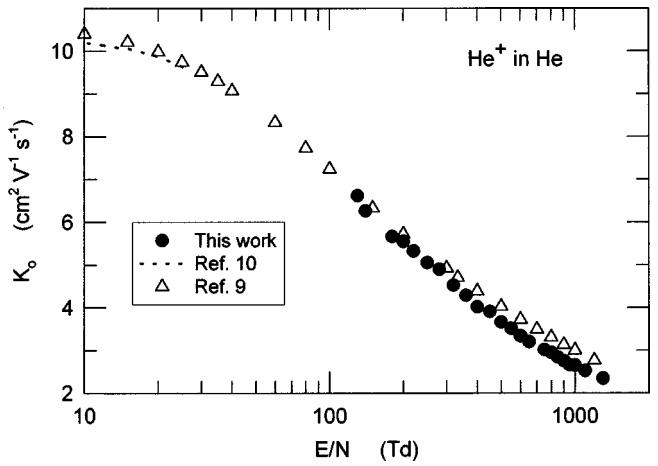

FIG. 2. Reduced mobility of He^+ in He as a function of E/N.

sidered, since only a few mean free paths would suffice to achieve whole relaxation. This region is terminated by a pair of flat, parallel, copper meshes that serve as ion shutters, and are intended for mobility measurements [6]. A means of assuring sufficient ion energy relaxation was the ease with which almost all ion flow into the drift space was stopped upon the application of a repeller voltage of less than 1 V between the shutter meshes.

After traversing the drift space, a sample of the drifting ions enters the ion detection chamber through a central orifice of 0.2 mm diameter, where a second QMS is followed by a continuous dynode multiplier, the output pulses of which are routed into a multichannel scaler, where an arrival time spectrum (ATS) is formed.

It has been shown [7] that for long drift distances (>5 cm) and relatively low-gas pressures (<50 Pa), the calculated mean, $\langle t \rangle$, of the ATS can be expressed to a very good approximation as

$$\langle t \rangle = z/v_d, \tag{1}$$

where z is drift distance, and v_d is ion drift velocity. Moreover, the movable ion source of the present apparatus provides a means of eliminating the so-called end effects by measuring the ATS at several source positions. From Eq. (1), a plot of $\langle t \rangle$ as a function of z would give a straight line, the slope of which is the inverse of v_d. At least four consecutive ion source positions were used to obtain each v_d.

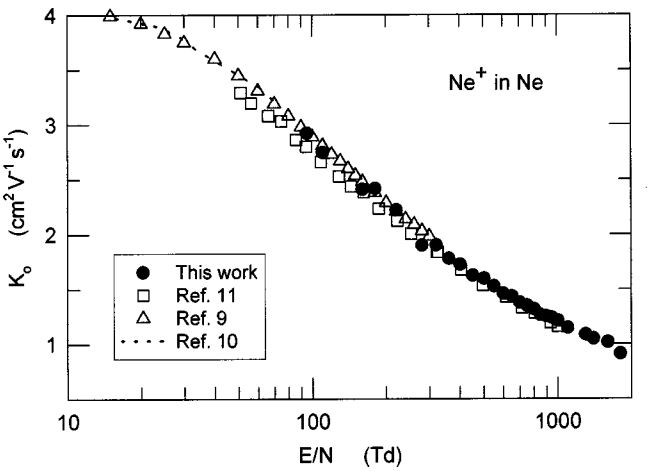

FIG. 3. Reduced mobility of Ne^+ in Ne as a function of E/N.

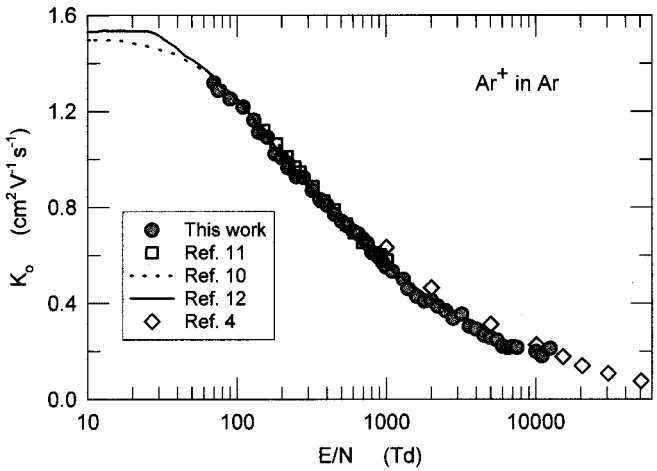

FIG. 4. Reduced mobility of Ar^+ in Ar as a function of E/N. The mobilities depicted by rhombs were derived from the measurement of the mean ion energy of Ar^+ in Ar [4].

The gas pressure in the drift chamber was controlled to within 0.3% of its set value by a servo valve coupled to a Baratron gauge with 0.05% full range accuracy. Drift distances could be read from a graduated scale to an accuracy of ± 0.5 mm. Two multichannel scalers (MCS) were used for the present measurement. A fast, 0.2 μs ($\pm$ 0.1 μs uncertainty) MCS was used to cover the higher E/N portion of the atomic ion species (>700 Td), and a 2 μs dwell time MCS (± 1 μs uncertainty) MCS was used for the rest of the measurements. Thus, for typical ion transit times in the range 0.5–3 ms, the instrumental errors in the drift velocity and the mobility ranged typically between 0.5–1.3 %. In most cases, the mobility measurement for a given E/N was performed at two or three different pressures. Therefore, the largest figure was considered as the final error.

Ultrahigh-purity grade (99.999%) nitrogen gas was used, while the other gases were quoted to be of high purity grade (>99.95%), and were injected into the drift chamber without further purification. All measurements were taken over the ambient temperature range 293–310 K for pressures between 0.66 and 20 Pa.

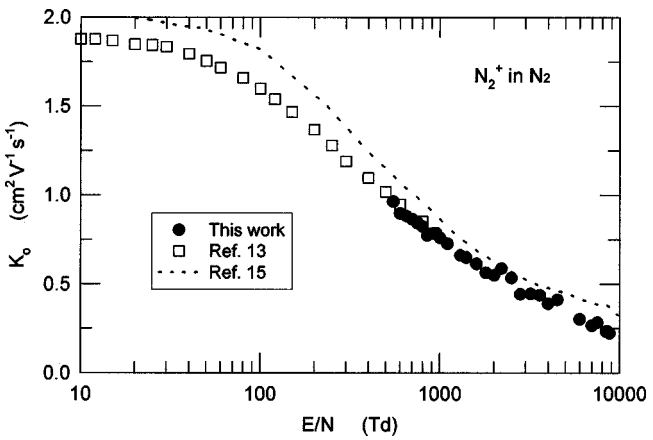

FIG. 5. Reduced mobility of N_2^+ in N_2 as a function of E/N.

TABLE I. Values of the fitting parameters of Eq. (3) for the ion mobility.

	He^+	Ne^+	Ar^+	N_2^+	O_2^+	CO_2^+
a	10.499	−0.107	0.105	.0876	−36.399	0.651
b	0.0260	−0.002	0.000145	−0.0000472	−0.050	0.000261
c	−0.223	0.017	−0.00143	0.000319	0.459	−0.00294
d	−93.43	33.17	20.76	24.29	1010.28	6.27
e	179.8	−13.734	−20.178	−15.42	−1551.9	−3.65
E/*N* range	130–1300	280–1800	110–12500	550–8800	130–1600	85–2500

III. RESULTS

Ion drift velocities were converted into reduced mobilities K_0 by the relation

$$K_0 = \frac{N}{N_0}\frac{\nu_d}{E}, \tag{2}$$

where $N_0 = 2.69\times10^{25}\,\mathrm{m}^{-3}$ is gas density at STP. Most of the data are the result of at least two measurements at different pressures, their overall accuracies ranging between 2 and 3%, and the error bars in the figures are contained within the symbols.

The mobilities of the atomic species He^+, Ne^+, and Ar^+ in their parent gases are shown plotted in Figs. 2–4 as a function of E/N, respectively. The E/N range of measurement for Ar^+ in Ar became remarkably wider than the other two because of the much easier control of the ions in the shutter meshes, and also because its mobility is substantially smaller than that of He^+ in He and Ne^+ in Ne. The lower end of the mobility measurements was dictated by either unsustainable high-gas pressures in the detection chamber, or by very low-ion count rates, due mainly to radial diffusion losses. Figures 5–7 display the mobility values for the polyatomic species N_2^+, O_2^+, and CO_2^+ in their parent gases as a function of E/N. In all cases, the E/N region that could be probed extensively was the high-field one, where the mobility follows a monotonic decline with E/N, and is a consequence of the predominance of the repulsive part (point charge-induced dipole) of the ion-neutral interaction potential.

Our mobility data can be well represented within quoted uncertainties by the function

$$K_0 = a + bx + cx(\ln x)^{-1} + dx^{-1/2} + ex^{-1}\ln x, \tag{3}$$

where $x = E/N$ in units of Td and K_0 is in units of $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. Values of the parameters *a* to *e*, and the ranges of validity for each ion-atom (molecule) species are given in Table I.

IV. DISCUSSION

Tables II and III summarize the relevant experimental work carried out in connection with our measurements, emphasizing the E/N ranges of investigation. It is seen that in all cases our experiment has either equalled or substantially exceeded the previous E/N limits of measurement. The pioneering work of Hombeck on the drift velocity of He^+, Ne^+, and Ar^+ in their parent gases [8], lacking mass spectrometry, is not discussed in this paper, since newer, mass analyzed data, are now available.

Values of the reduced mobility of He^+ in He are in good agreement with those of Helm [9] only at the beginning of the overlap range, but then ours become systematically smaller. Although he used a drift tube without mass analysis, his data leave no question as to identity of the ion. Even though the other set of mass-analyzed mobilities of Beaty and Patterson [10] at low E/N is well outside our measurement range, we have considered important to display all these data, since they now provide a very wide, useful range of measurement, extending over several decades of E/N.

The above discussion also applies to the mobilities of Ne^+ in Ne, where the present range of measurement almost doubled that reached by Hegerberg, Elford, and Skullerud [11] and of Helm [9]. It is worth noticing the excellent agree-

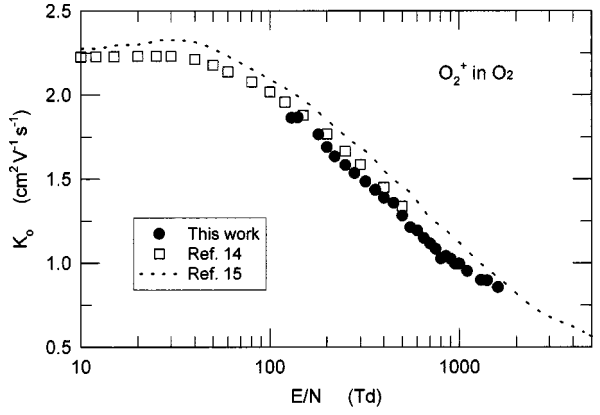

FIG. 6. Reduced mobility of O_2^+ in O_2 as a function of E/N.

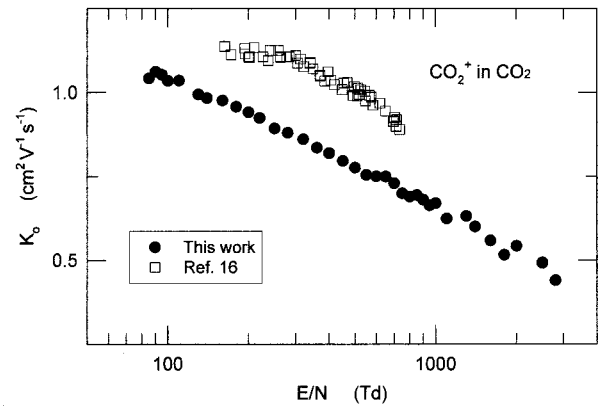

FIG. 7. Reduced mobility of CO_2^+ in CO_2 as a function of E/N.

TABLE II. Ranges of E/N (Td) measurement of the ion mobility for the atomic species.

Author	He^+	Ne^+	Ar^+
Beaty	4–27	5–73	7–216
Helm	10–1200		
Hegerberg		50–1000	150–1000
Hornbeck	21–770	27–1700	60–2200
this work	130–1300	280–1800	110–12500

TABLE III. Ranges of E/N (Td) measurement of the ion mobility for the polyatomic species.

Author	N_2^+	O_2^+	CO_2^+
Moseley	6–800		
Snuggs		4–500	
Saporosch.			160–730
this work	550–8800	130–1600	85–2500

ment of our data with those of Helm, in the overlap range, in contrast with the case of He^+ in He.

Of particular relevance is the present measurement of Ar^+ in Ar, extending up to 12.5 kTd, which is a factor of about six higher than the widest one so far reported. The recent Townsend experiment of Rao, Van Brunt, and Olthoff [4], dealing with the study of diffuse discharges in He, Ne, and Ar at very high E/N ratios enabled these authors to measure the translational kinetic-energy distributions of these ions in their parent gas over the E/N range 1–50 kTd, from which the mean energy $\langle\varepsilon\rangle$ of the ion swarm could be determined, and consequently the ion drift velocity by the formula [4]

$$\langle\varepsilon\rangle = \frac{\pi}{2} M \nu_d^2, \tag{4}$$

where M is the ion mass. For the particular case of Ar^+ in Ar, where there is an overlap between the E/N values of these authors and those presented here, we found that the agreement between our Ar^+ mobility values and those derived from Eq. (4) is pretty good, mostly above 10 kTd, where both mobility values almost overlap, as is seen in Fig. 4. Furthermore, for $E/N > 12$ kTd, the mobility values derived from the mean energies of Rao, Van Brunt, and Olthoff are a smooth continuation of the whole mobility curve, up to 50 kTd. This excellent agreement would validate the simple model used in Ref. [4] to analyze the ion-energy measurements using the Townsend method. On the theoretical side, the recent Monte Carlo calculations of Hennad *et al.* [12] seem to be in excellent agreement with our measurements.

Again, as for the case of the atomic species, the present ranges of measurement of the polyatomic ions extend well beyond those hitherto reported, particularly in the case of N_2^+ in N_2, which extends a factor of ten the previous limit reached by Moseley *et al.* [13]. For N_2^+ in N_2 and O_2^+ in O_2, in general, the overlap with the values of this author and with Snuggs *et al.* [14], respectively, is excellent. In this case, the calculated mobilities of Kanzari, Yousfi, and Homani [15] for these two systems are slightly higher than ours. As regards the mobility of CO_2^+ in CO_2, the mobility measurements of Saporoschenko [16] disagree strongly from ours. We know of no further measurements on the mobility of this important ion in atmospheric and environmental physics.

V. CONCLUSIONS

The addition of a mass spectrometer to the ion source of our drift tube has permitted the successful measurement of the mobility of the above six species in their parent gases over a wide-E/N range, covering ranges hitherto unexplored. On the grounds that resonant charge transfer is the predominant interaction mechanism, it was confirmed that the ions as formed in the ion source, relax their excess energy very efficiently, thereby drifting under well-established equilibrium conditions. It is hoped that the present data, together with previous data, many of them at low or intermediate E/N, would now constitute a mobility set with which interaction potentials and resonant charge transfer cross sections could be derived over a wide energy range. In view of the excellent agreement between the present mobility values and those inferred from the mean ion energy measured in diffuse Townsend discharges, it seems that the latter method is very successful and unique for studying ion transport at very high values of E/N.

ACKNOWLEDGMENTS

This project was partially supported by DGAPA IN 113898. Thanks are due to A. Bustos for his technical assistance.

[1] E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).

[2] E. W. McDaniel, J. B. A. Mitchell, and M. Eugene Rudd, *Atomic Collisions: Heavy Particle Projectiles* (Wiley, New York, 1993).

[3] H. W. Ellis, R. Y. Pai, E. W. McDaniel, E. A. Mason, and L. A. Viehland, At. Data Nucl. Data Tables **17**, 177 (1976); H. W. Ellis, E. W. McDaniel, D. L. Albritton, L. A. Viehland, S. L. Lin, and E. A. Mason, *ibid.* **22**, 179 (1978); H. W. Ellis, M. G. Thackston, E. W. McDaniel, and E. A. Mason, *ibid.* **31**, 113 (1978); L. A. Viehland and E. A. Mason, *ibid.* **60**, 37 (1995); A. V. Phelps, J. Phys. Chem. Ref. Data **20**, 557 (1991).

[4] M. V. V. S. Rao, R. J. Van Brunt, and J. K. Olthoff, Phys. Rev. E **54**, 5641 (1996); S. B. Radovanov, R. J. Van Brunt, J. K. Olthoff, and B. M. Jelenkovic, *ibid.* **51**, 6036 (1995).

[5] V. T. Gylys, B. M. Jelenkovic, and A. V. Phelps, J. Appl. Phys. **65**, 3369 (1989).

[6] J. de Urquijo, I. Alvarez, C. Cisneros, and H. Martínez, J. Phys. D **23**, 778 (1990).

[7] J. de Urquijo, I. Alvarez, C. Cisneros, and H. Martínez, Int. J. Mass Spectrom. Ion Processes **154**, 25 (1996).

[8] J. A. Hornbeck, Phys. Rev. **84**, 615 (1951).

[9] H. Helm, J. Phys. B **10**, 3683 (1977).
[10] E. C. Beaty and P. L. Paterson, Phys. Rev. **137**, 346 (1965).
[11] R. Hegerberg, M. T. Elford, and H. R. Skullerud, J. Phys. B **15**, 797 (1982).
[12] A. Hennad, O. Eichwald, M. Yousfi, and O. Lamrous, J. Phys. III **7**, 1877 (1997).
[13] J. T. Moseley, R. M. Snuggs, D. W. Martin, and E. W. McDaniel, Phys. Rev. **178**, 240 (1969).
[14] R. M. Snuggs, D. J. Volz, J. H. Schummers, D. W. Martin, and E. W. McDaniel, Phys. Rev. A **3**, 477 (1971).
[15] Z. Kanzari, M. Yousfi, and A. Hamani, J. Appl. Phys. **84**, 4161 (1998).
[16] M. Saporoschenko, Phys. Rev. A **8**, 1044 (1973).