

Mobilities of doubly charged rare-gas ions in their parent gases

Rainer Johnsen and Manfred A. Biondi

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 5 May 1978)

The mobilities of the doubly charged rare-gas ions He^{2+} , Ne^{2+} , Ar^{2+} , Kr^{2+} , and Xe^{2+} in their parent gases have been determined in a drift-tube mass-spectrometer apparatus. The finding of more than one mobility for each of the doubly charged ions (with the exception of He^{2+}) is attributed to the presence of the 3P , 1D , and 1S long-lived, lowest-energy states of these ions. At 300 K the reduced mobilities (in units of cm^2/Vsec) extrapolated to zero field have the values $\mu_0(\text{He}^{2+} \text{ in He}) = 18.3$; $\mu_0(\text{Ne}^{2+} \text{ in Ne}) = 6.5(^1D)$, $7.0(^3P)$, $8.5(^1S)$; $\mu_0(\text{Ar}^{2+} \text{ in Ar}) = 2.7(^3P)$, $\sim 2.2(^1D)$; $\mu_0(\text{Kr}^{2+} \text{ in Kr}) = 1.11$ and 1.28 ; $\mu_0(\text{Xe}^{2+} \text{ in Xe}) = 0.65$ and 0.75 . The measured values are accurate to $\pm 3\%$.

I. INTRODUCTION

The mobilities of rare-gas ions in their parent gases have been the subject of numerous experimental and theoretical investigations, and their study has contributed significantly to our understanding of ion-atom interactions and charge-transfer processes. Somewhat surprisingly, little attention has been paid to the doubly charged ions. With the exception of Ar^{2+} in Ar,¹⁻³ no systematic studies appear to have been undertaken of the mobilities of these ions or of their reactions with rare gas atoms.

In the course of an investigation of the reaction kinetics of these ions in their parent gases (see following paper⁴) we have measured their mobilities in a drift-tube mass-spectrometer apparatus. We find that the mobilities of the doubly charged rare-gas ions R^{2+} depend quite strongly on the state of excitation of the ions. With the obvious exception of He^{2+} , the electronic configuration of their lowest states is analogous to that of atomic oxygen, i.e., four p electrons interact to produce a $^3P_{2,1,0}$ ground state and two low-lying, metastable excited states a 1D and a 1S state. The calculated lifetimes of the excited states^{5,6} are sufficiently long compared to the ion transit times in the drift tube that accurate mobility values for each of the states can be determined.

II. EXPERIMENTAL METHOD

The measurements were carried out in a drift-tube mass-spectrometer apparatus which was designed primarily for measurements of ion-molecule reaction rates. A simplified drawing of the apparatus is shown in Fig. 1. The ions are generated from their parent gases in a differentially pumped, electron-impact ion source at electron energies ranging typically from 50 to 200 eV. Pulsing of the ion source is achieved by applying a short (2–10 μsec) negative voltage pulse to the

ionizer filaments which are normally biased so that the electrons have insufficient energy to ionize. The parent gas enters the ion source through a narrow capillary (and also through the injection orifice from the drift tube which, for these studies, is filled with parent gas). The ion drift velocity is determined from the transit time of a pulse of ions across the drift region and is measured as a function of E/N , the ratio of the drift electric field to the gas density in that region.

The ions typically enter the drift region with an energy of 20–40 eV, depending on the bias voltage of the ion source with respect to the injection orifice. Because of this excess energy the ions may penetrate a short distance into the drift region, in effect reducing the drift distance slightly below its physical length of 36.2 cm, measured between the injection and sampling (exit) orifices. The effect is most pronounced for ions of high mobility (e.g., He^{2+} in He) and at low gas pressures (see Sec. III A). A uniform electric field is generated in the drift region by applying appropriate voltages to the series of cylindrical electrodes. While small non-uniformities in the field may exist in the vicinity of the entrance and exit electrodes, the effect on the measured mobilities is of second order.

After transiting the drift region, some of the ions in the swarm effuse through the sampling orifice into the differentially pumped quadrupole mass filter and channel electron multiplier. The resulting ion counts are stored in a multichannel analyzer operated in a time-of-flight mode synchronized by the ion source trigger pulse. By coherently summing counts over many cycles of the experiment, an accurate reproduction of the ions' arrival spectrum is obtained. The time of occurrence of the maximum in this arrival spectrum is used to compute the drift velocity (ion mobility) rather than the more accurate "average arrival time," the difference being of the order of $\frac{1}{2}\%$. In view of other sources of uncertainties, the more rigorous analysis⁷ does not seem justified.

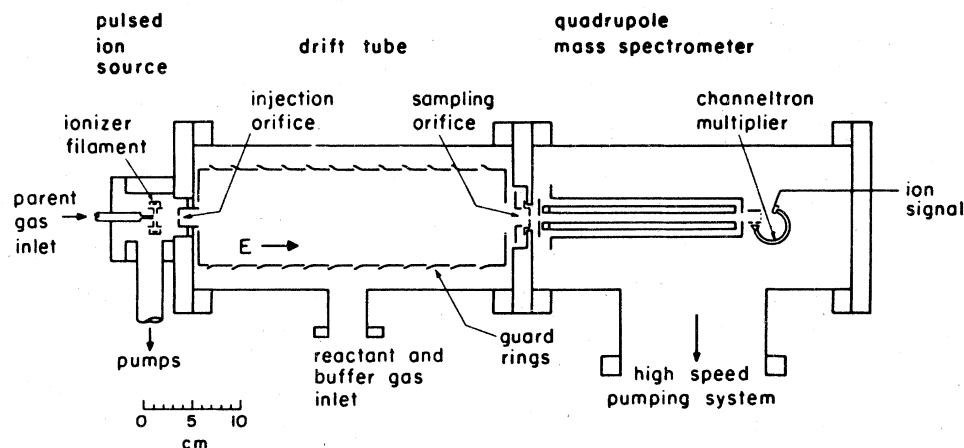


FIG. 1. Simplified scale drawing of the drift-tube mass-spectrometer apparatus.

The gas pressures were determined by a sensitive capacitance manometer (MKS Baratron Model 90) calibrated against a mercury McLeod gauge. The gases used were ultrahigh-purity samples (He, Ar, and Xe from Matheson Co., Ne from Linde Corp., and Kr from Precision Gas Products, Inc.) and, except for the use of dry-ice- or liquid-nitrogen-cooled traps, no further purification was found necessary. The gas temperature in these experiments ranged from 300 to 306 K. Following the usual convention, the measured mobilities have been reduced to values at the standard density of $2.69 \times 10^{19} \text{ cm}^{-3}$.

III. RESULTS AND DISCUSSION

A. He^{2+} in He

Some difficulty was encountered in producing an adequate He^{2+} ion signal; at electron impact energies of 200 eV, the He^{2+} ion current was only about 0.1% of the He^+ current. Fortunately, confusion of the He^{2+} ion with H_2^+ (a possible, but unlikely impurity ion having the same mass-to-charge ratio) can be discounted. The high appearance potential of the ion under study, its ability to produce He^+ ions by charge transfer, and the absence of production of H_3^+ ions leave little doubt that the identification of the "mass-2" ion as He^{2+} is correct.

The measured mobilities are shown in Fig. 2 as a function of E/N for several gas pressures. The data displayed in Fig. 2 were taken under conditions so that the ions were injected into the drift tube with an energy of 40 eV. To evaluate possible injection effects, data were taken at high injection energies (~ 160 eV), yielding mobilities that were about 5% higher at low gas pressures (0.2 Torr) than those given in Fig. 2. While it was not possible to eliminate this injection effect complete-

ly, we estimate that mobilities deduced from the 0.25-Torr data should be $\leq 2\%$ high, while for data taken at the higher pressures the error should be $\leq 1\%$.

Ions in helium with mobilities of about $20 \text{ cm}^2/\text{V sec}$ have been observed previously in experiments lacking mass analysis of the ions.⁹⁻¹¹ While some authors¹² assigned this mobility to the He^{2+} ion, a later suggestion¹³ that the ion under study was He_2^+ in a metastable state received some acceptance. This argument was strengthened by the apparent observation of an ion of mass-to-charge ratio of 8 having this mobility¹⁴ in an experiment employing mass analysis. We have repeatedly tried to produce the metastable He_2^+ ion in the present electron-impact ion source, and in earlier measurements using pulsed discharge sources, but have failed to observe it.

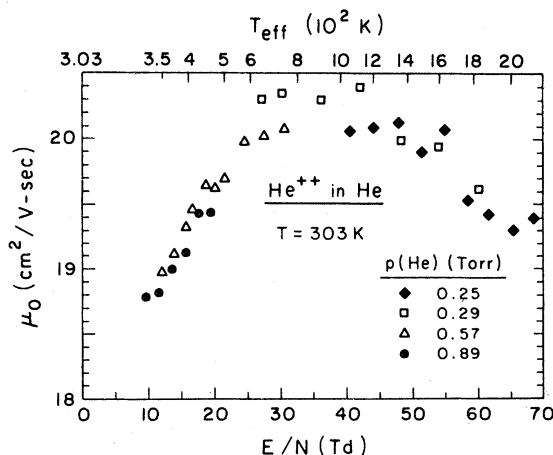


FIG. 2. Measured reduced mobilities μ_0 for He^{2+} ions in helium as a function of E/N ($1 \text{ Td} = 10^{17} \text{ V cm}^{-2}$) at $T = 303 \text{ K}$ for several helium pressures.

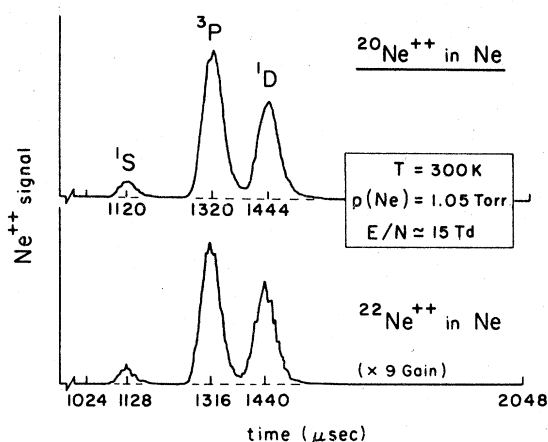


FIG. 3. Observed arrival time spectra for Ne^{2+} ions in neon at $p=1.05$ Torr, $T=306$ K, and $E/N \approx 15$ Td, showing 3 distinct ionic mobilities. Results are shown for both isotopes, ^{20}Ne ($\sim 91\%$) and ^{22}Ne ($\sim 9\%$).

B. Ne^{2+} in Ne

The arrival time spectra of Ne^{2+} ions in neon are found to have the shapes shown in Fig. 3. At pressures above 0.3 Torr, three peaks are clearly distinguishable at moderate values of E/N , and for both of the isotopes $^{20}\text{Ne}^{2+}$ and $^{22}\text{Ne}^{2+}$, the relative amplitudes and transit times are found to be the same, within experimental error. As will be shown, these distinct mobilities are associated with Ne^{2+} ions in different electronic states, the $^3P_{2,1,0}$ ground state, and the low-lying metastable 1D and 1S states.

Varying the electron energy in the ion source causes changes in the relative amplitudes of the three peaks. The first peak (highest mobility) is the first to disappear as the electron-impact energy is reduced, indicating that it results from the

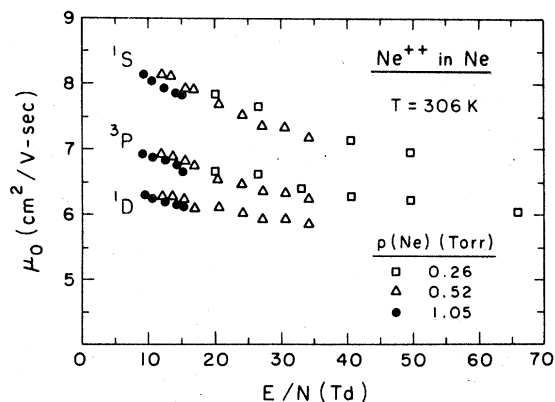


FIG. 4. Reduced mobilities for Ne^{2+} ions in neon as a function of E/N at 306 K, showing the effect of the ionic state on the mobility.

1S (highest-energy) state. The third peak is the next to decrease strongly with decreasing electron energy, leading to its assignment as 1D . The middle peak is therefore associated with the 3P ground state.

The measured mobilities for the three Ne^{2+} ionic states are given in Fig. 4. The range of E/N values for which measurements are shown is somewhat limited, since at high E/N values and low neon pressures the three arrival-time spectra begin to overlap, making it difficult to assign proper transit times. While some of this overlap is the result of increased diffusion broadening at low gas pressures, it also appears that at higher energies the differences in ionic mobilities for the different states become smaller.

C. Ar^{2+} in Ar

At pressures above ~ 0.2 Torr only one mobility peak was observed for Ar^{2+} ions drifting through argon gas. At pressures below 0.2 Torr a second peak was seen at longer transit times, considerably smaller in magnitude and partially overlapping the first peak (see Fig. 5). The dependence of the relative peak heights on the electron energy in the ion source suggests that the second peak belongs to an excited state of Ar^{2+} , probably the 1D state. An estimate of its mobility over a small range of E/N is included in Fig. 6, which shows the measured mobilities for three different argon pressures as a function of E/N . The main mobility peak probably corresponds to ions in the 3P state.⁴

Mobilities of Ar^{2+} ions in argon have been investigated by Beaty¹ in measurements without mass analysis. The ion was identified in later studies using mass analysis by McAfee *et al.*² and by Madson and Oskam.³ Beaty's data are shown by the dashed line in Fig. 6. Under Beaty's experimental conditions of higher argon pressures, only the 3P state of Ar^{2+} should have been present.

No indication of a third peak, analogous to the

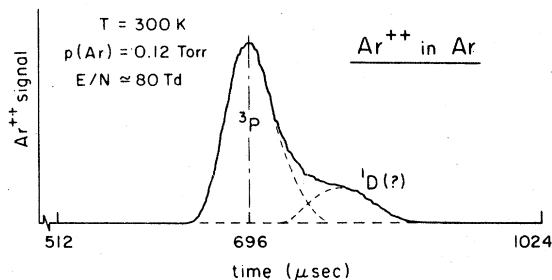


FIG. 5. Observed arrival time spectra for Ar^{2+} ions in argon at $p=0.12$ Torr, $T=300$ K, and $E/N \approx 80$ Td, showing two distinct mobilities associated with the 3P and probably the 1D states of the ion.

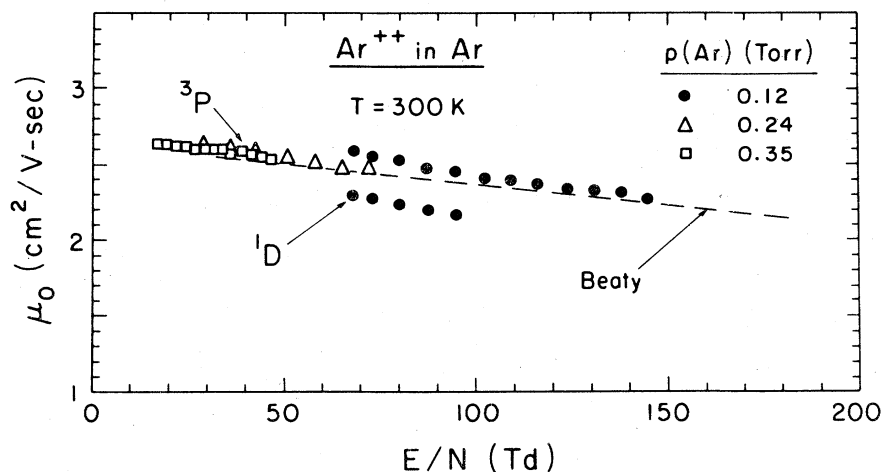


FIG. 6. Reduced mobilities for Ar^{2+} ions in argon as a function of E/N at 300 K. The dashed line represents the measurements of Beatty, which did not involve mass analysis.

^1S peak for Ne^{2+} in neon, was observed in argon. From studies of Ar^{2+} ions drifting in helium buffer gas to which small amounts ($\leq 1\%$) of argon are added, it appears that single-electron charge transfer of Ar^{2+} ions with Ar is very fast for ^1S state ions, rather slower for ^1D -state ions (accounting for their observability in pure argon at low pressures), and slowest for ^3P ground-state ions (see following paper⁴). Thus in pure argon, the ^1S state of Ar^{2+} would be destroyed so rapidly as to be unobservable.

D. Kr^{2+} in Kr

Two distinctly different mobilities were observed for Kr^{2+} ions in Kr. The first peak in the arrival spectrum was about 20%–30% larger than the second at 160 eV electron-impact energy, but its relative intensity was reduced at low electron energy (~ 10 eV above threshold). The relative sizes of the two peaks were independent of gas pressure and transit time. The identification of the two

peaks in terms of the states of the Kr^{2+} ions is unclear. There was some indication that only a fraction of the ions contained in the first peak react with Xe, suggesting that the first peak contains a mixture of states.

The measured mobilities are shown in Fig. 7, with the two Kr^{2+} groups identified simply as A and B. Since we found that Kr^{2+} ions were produced in very large numbers in our ion source (about 20% of the Kr^+ current), it seems likely that the ion was present in earlier mobility studies in krypton but was not recognized as such. The ion with a mobility of $1.2 \text{ cm}^2/\text{V sec}$ observed by Biondi and Chanin,⁷ then thought to be due to Kr_2^+ , probably resulted from their inability to resolve the transit times of the two Kr^{2+} ions observed in the present experiment. Their data also exhibit the same very weak dependence of μ_0 on E/N that we find for Kr^{2+} ions. We have observed Kr_2^+ ions in the present experiment and find that their mobility is $\sim 1.0 \text{ cm}^2/\text{V sec}$, about 10% smaller than that of Kr^{2+} (B).

We note in passing that for singly charged ions the

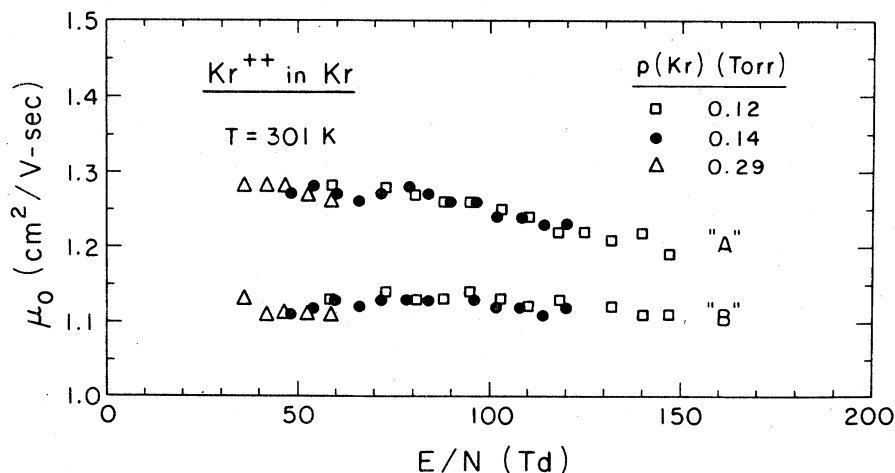


FIG. 7. Reduced mobilities for Kr^{2+} ions in krypton at 301 K, showing two ionic groups (see text for discussion).

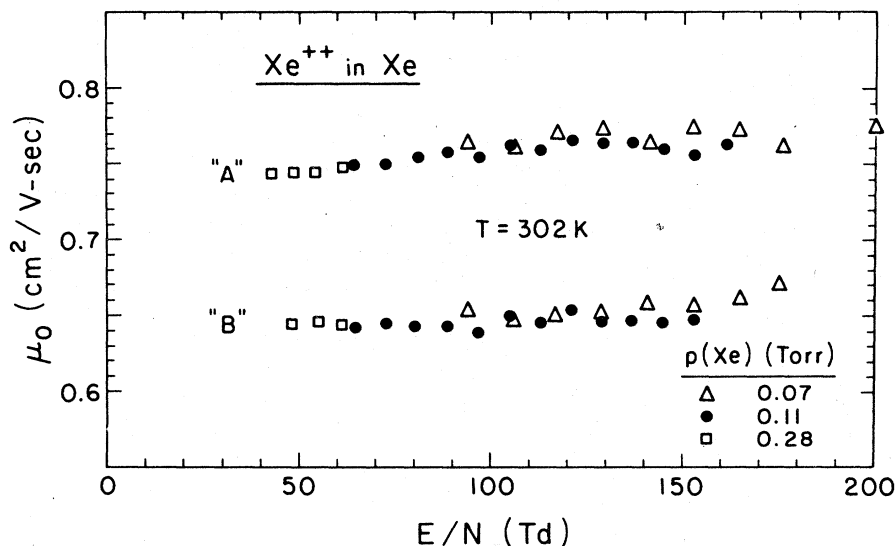


FIG. 8. Reduced mobilities for Xe^{2+} ions in xenon at 302 K, showing two ionic groups (see text for discussion).

difference between the mobilities of Kr^+ ions in the $^2P_{1/2}$ and the $^2P_{3/2}$ states reported by Helm¹⁵ has also been observed in the present studies.

E. Xe^{2+} in Xe

Two distinctly different mobilities were observed for Xe^{2+} ions in xenon. The peak (B) corresponding to the lower mobility is quite small, about 5%–10% of the faster-ion peak (A). The variation of peak heights with the electron energy in the ion source indicates that the B peak contains ions in energetically higher states than does the A peak. The measured mobilities are displayed in Fig. 8. From these results it seems probable that the ion observed in earlier work⁹ without mass analysis and identified as Xe_2^+ was actually Xe^{2+} , since the reported mobility, $\sim 0.75 \text{ cm}^2/\text{V sec}$, is close to that of the more abundant Xe^{2+} (A) ions. An ion with $\mu_0 = (0.72 \pm 0.02) \text{ cm}^2/\text{V sec}$ has been observed by Helm¹⁶ in an experiment without mass analysis, and was tentatively identified as Xe^{2+} , in agreement with the present results. Unfortunately, Xe_2^+ could not be studied in the present experiment because its mass exceeded the upper limit of our quadrupole mass filter.

As in the case of krypton, studies of the singly charged ion show the two distinct mobilities for Xe^+ ions in xenon reported by Helm.¹⁷ These presumably correspond to the two ionic ground states, $^2P_{3/2}$ and $^2P_{1/2}$.

F. Doubly charged rare-gas ions R^{2+} in He

In order to obtain more information concerning the mobility and reactivity of the different electronic states of the doubly charged rare-gas ions, studies were carried out in helium and in helium-

other-rare-gas mixtures. Tests were performed to see if the R^{2+} ions retained their identities long enough in helium for mobility measurements to be carried out. All of the ions survived drift through pure helium at pressures of ~ 1 Torr and transit times on the order of 10^{-3} sec; however, in no case was a splitting of the arrival time spectra into distinctly different mobility peaks apparent. In the case of Ar^{2+} , it appears that the presence of only one peak is due to reactive loss of all but one of the ionic states. Ne^{2+} ions were found to exhibit the same three mobility peaks in helium-neon mixtures (30% He, 70% Ne) that were seen in pure neon, but with smaller separations between the peaks. Thus the single mobility peak of Ne^{2+} ions in helium probably contains ions in all three states. It is found that the mobilities of R^{2+} ions in helium are rather close to those of their singly charged counterparts.

IV. CONCLUSIONS

The present paper has presented determinations of the mobilities in their parent gases of doubly charged rare-gas ions in various electronic states. While every attempt has been made to measure critical parameters, e.g., gas pressures, voltages, etc., precisely, the accuracy of mobility determinations in drift-tube mass spectrometers of fixed length may still be limited by other effects, some of which have been discussed by McDaniel.⁷ Summarily referred to as "end effects," errors may arise from sources such as nonuniformities in the electric field near the entrance and exit electrodes of the drift tube, nonequilibrium drift motion of the ions at injection, and small time delays in injection from the ion source. The influ-

ence of these effects on the deduced mobilities is difficult to calculate. Instead we have used experimental tests, such as varying the ion injection energy and the gas pressure, to evaluate effects on the ion transit times and have remeasured well-known mobilities (e.g., Ne^+ in Ne) to determine that the overall experimental error in the deduced mobilities is $\leq 3\%$. It appears that mobilities measured in our type of apparatus have a tendency to be systematically too high.

The results of the measurements are summarized in Table I, where the zero-field mobilities, obtained by extrapolation of the data to $E/N=0$, are listed. The extrapolations are most accurate for Ar^{2+} , Kr^{2+} , and Xe^{2+} , whose mobilities were found to be nearly independent of E/N . The experimental values are compared with the Langevin mobilities, calculated on the assumption that the only significant ion-atom interaction is the long-range polarization attraction between a point ion and a polarizable atom. The reduced mobility μ_0 (referred to a standard gas density of $2.69 \times 10^{19} \text{ cm}^{-3}$) is calculated from the relationship¹⁸

$$\mu_0(\text{cm}^2/\text{V sec}) = 35.9[m_r \alpha(a_0^3)]^{-1/2}, \quad (1)$$

where m_r is the reduced mass and α is the atomic polarizability.

It will be seen that there is fair agreement between our measured values and this simple theory. Furthermore, the very weak dependence on ion energy noted for the Ar^{2+}/Ar , Kr^{2+}/Kr , and Xe^{2+}/Xe mobilities is consistent with the Langevin prediction of a mobility independent of energy. The differing mobilities for the different electronic states of a particular species of rare-gas ion are explicable in terms of differing interactions at shorter range.

In the case of He^{2+} in He, Dickinson¹⁹ has calculated the mobility quantum mechanically using po-

tential curves for the lowest $^1\Sigma_u^+$ and first excited $^1\Sigma_g^+$ state of He_2^{2+} , obtained from calculations by Browne²⁰ for small separations (≤ 6 a.u.) and joined smoothly to the asymptotic polarization terms for larger separations. Dickinson finds that, from a minimum value of $22.6 \text{ cm}^2/\text{V sec}$ at 20 K, the mobility rises to a maximum value of 23.2 at 80 K and then falls monotonically with further increase in temperature (at 303 K, the value 20.5 is obtained, some $\sim 10\%$ higher than our experimental results).

To facilitate a comparison with these predictions, we have added an effective temperature (T_{eff}) scale to the top of Fig. 2, using the Wannier relationship²¹ to relate the mean relative energy between ions and atoms to an effective temperature, viz.,

$$\frac{3}{2} kT_{\text{eff}} = \frac{3}{2} kT_{\text{gas}} + \frac{1}{2} m_{\text{He}} v_{\text{drift}}^2. \quad (2)$$

(The mobility is not particularly sensitive to differences between the actual ion-atom velocity distribution and the Maxwellian distribution implied by the introduction of an effective temperature.) It will be seen from Fig. 2 that the measured mobility increases with T_{eff} above 303 K, reaching a maximum value of 20.3 at $T_{\text{eff}} \sim 900$ K and then decreases with further increase in T_{eff} . This behavior is quite different from the theoretical predictions of Dickinson.

In view of the relative simplicity of the He^{2+} -He system, the difference between theory and experiment concerning the energy dependence of the mobility is somewhat surprising. Very recently the potential energy curves of the He_2^{2+} system have been recalculated by Cohen and Bardsley as part of a theory of radiative charge transfer.²² Using these new potential curves Wadehra and Bardsley²³ have just completed calculations of μ_0 (He^{2+} in He) and obtain excellent agreement with our experimental results, reproducing the shape of the mo-

TABLE I. Reduced mobilities μ_0 (in units of $\text{cm}^2/\text{V sec}$) of the doubly charged rare-gas ions in their parent gases at $T \approx 300$ K.

| Ion/gas | Polarizability ^a | μ_0 (Langevin theory) | μ_0 (Present experiment) |
|---------|-----------------------------|---------------------------|--|
| | $\alpha[a_0^3]$ | | |
| helium | 1.38 | 21.6 | 18.3 |
| neon | 2.67 | 6.95 | 6.5(¹ D) 7.0(³ P) 8.5(¹ S) |
| argon | 11.08 | 2.41 | 2.7(³ P) ~ 2.2 (¹ D) |
| krypton | 16.75 | 1.35 | 1.11("B") 1.28("A") |
| xenon | 27.29 | 0.85 | 0.65("B") 0.75("A") |

^aReference 7.

bility curve given in Fig. 2. The experimental values are systematically ~5% higher than the theoretical values; part of this difference may arise from the fact that our method tends to lead to a slight overestimate of the actual mobilities.

ACKNOWLEDGMENT

This research was supported in part by the Army Research Office under Contract No. DAA-G-29-77G-0079.

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- ¹E. C. Beaty, Phys. Rev. 104, 473 (1956).
²K. B. McAfee, Jr., D. Sipler, and D. Edelson, Phys. Rev. A 160, 130 (1967).
³J. M. Madson and H. J. Oskam, Phys. Lett. 25, A, 407 (1967).
⁴R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978), following paper.
⁵R. H. Garstang, Mon. Not. R. Astron. Soc. 111, 115 (1951).
⁶R. H. Garstang, J. Res. Natl. Bur. Stand. A 68, 61 (1964).
⁷See, for example, E. W. McDaniel and E. A. Mason, *The Mobility and Diffusion of Ions in Gases* (Wiley, New York, 1973) and the references cited therein.
⁸A. M. Tyndall and C. F. Powell, Proc. R. Soc. Lond. A 134, 125 (1931).
⁹M. A. Biondi and L. M. Chanin, Phys. Rev. 94, 910 (1954).
¹⁰E. C. Beaty and P. L. Patterson, Phys. Rev. 137, 346 (1965).
¹¹O. J. Orient, Can. J. Phys. 45, 3915 (1967).
¹²M. A. Biondi and S. C. Brown, Phys. Rev. 75, 1700 (1949).
¹³E. C. Beaty, J. C. Browne, and A. Dalgarno, Phys. Rev. Lett. 16, 723 (1966).
¹⁴J. M. Madson, H. J. Oskam, and L. M. Chanin, Phys. Rev. Lett. 15, 1018 (1965).
¹⁵H. Helm, Chem. Phys. Lett. 36, 97 (1975).
¹⁶H. Helm, Phys. Rev. A 14, 680 (1976).
¹⁷H. Helm (private communication).
¹⁸H. S. W. Massey, *Electronic and Ionic Impact Phenomena* (Clarendon, Oxford, 1971), Vol. 3, p. 1961.
¹⁹A. S. Dickinson, J. Phys. B 1, 395 (1968).
²⁰J. C. Browne, J. Chem. Phys. 42, 1428 (1965).
²¹G. H. Wannier, Bell Syst. Tech. J. 32, 170 (1953).
²²J. Cohen and J. N. Bardsley, Phys. Rev. A 18, 1004 (1978), accompanying paper.
²³J. M. Wadehra, J. S. Cohen, and J. N. Bardsley, Phys. Rev. A 18, 1009 (1978).