PHYSICAL REVIEW A VOLUME 18, NUMBER 3 SEPTEMBER 1978

Measurements of radiative charge-transfer reactions of doubly and singly charged rare-gas ions with rare-gas atoms at thermal energies

Rainer Johnsen and Manfred A. Biondi
Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 5 May 1978)

Radiative charge-transfer coefficients for single-electron transfer between doubly or singly charged noble-gas ions and noble-gas atoms have been determined at thermal energy using a drift-tube mass-spectrometer apparatus. At 300 K, $k(\mathrm{He}^{2+} + \mathrm{He}) = (4.8 \pm 0.5) \times 10^{-14}$ cm^3/sec, with slightly smaller coefficients for the reactions $\mathrm{Ne}^{2+} + \mathrm{Ne}$, $\mathrm{Ar}^{2+} + \mathrm{Ar}$, $\mathrm{Kr}^{2+} + \mathrm{Kr}$, and $\mathrm{Xe}^{2+} + \mathrm{Xe}$. Differences in reactivity are found for the different, low-lying ^1S, ^1D, and ^3P states of the doubly charged ions. A three-boby contribution to the radiative process is noted, with rate coefficients ranging between 10^{-31} and 10^{-30} cm^6/sec at 300 K for the different noble-gas systems. The radiative charge-transfer coefficients for singly ionized ions are somewhat smaller, $k(\mathrm{He}^+ + \mathrm{Ne}) \sim 1 \times 10^{-15}$ cm^3/sec and $k(\mathrm{Ne}^+ + \mathrm{Ar}) \sim 6 \times 10^{-15}$ cm^3/sec at 300 K. The measured value of $k(\mathrm{He}^{2+} + \mathrm{He})$ is in reasonable agreement with the very recent theoretical calculations of Cohen and Bardsley.

I. INTRODUCTION

At low energies, nonresonant charge-transfer processes of the type

$$X^{n+} + Y \to X^{(n-1)+} + Y^{+} (+ h\nu) \tag{1}$$

can proceed in two distinct ways. A nonradiative transition to the final state may take place at a crossing or avoided crossing of the potential curves describing the initial and final states of the system, as illustrated in Fig. 1(a). Alternatively, if no crossings are energetically accessible and selection rules permit, a radiative transition between initial and final states may take place during the collision, as illustrated in Fig. 1(b). Since the duration of this collision is very short (10^{-14}–10^{-13} sec) compared to the radiative lifetime ($\sim 10^{-8}$ sec) of the unbound state U of the molecule formed during the collision, the probability of occurrence of the radiative process is inherently small.

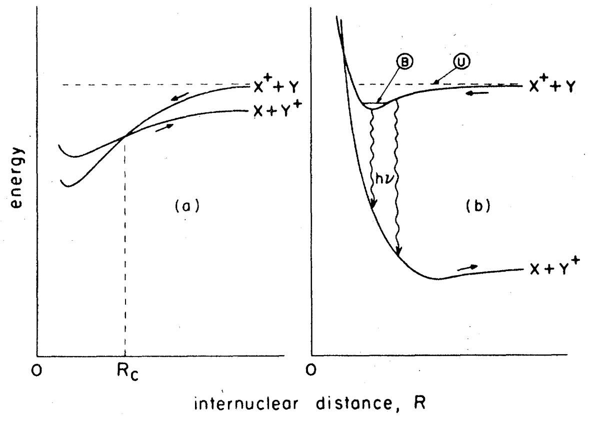

FIG. 1. Schematic potential energy curves illustrating nonresonant charge transfer (a) by a nonradiative transition at a curve crossing or avoided crossing between initial and final states, and (b) by a radiative transition from the initial to the final state.

At moderate neutral atom densities the radiative process can be enhanced by formation of a bound upper state [B in Fig. 1(b)] as a result of an energy-removing collision with a third body. Once formed, the bound upper state has ample time to radiate to the lower, final state of the system. This three-body process may be termed associative-radiative charge transfer.

Our previous studies of nonresonant charge-transfer[1,2] at low energies involved atomic systems in which accessible curve crossing between initial and final states were expected. This paper describes what are believed to be the first experimental studies of a number of radiative charge transfer reactions of doubly and singly charged rare-gas ions with rare-gas atoms.

II. EXPERIMENTAL APPARATUS AND TECHNIQUE

With the exception of the low-temperature studies of $\mathrm{Ar}^{2+} + \mathrm{Ar}$, all measurements have been carried out in the same drift-tube mass-spectrometer apparatus used in the mobility studies described in several earlier studies of ion-molecule reactions[1,2] and in the preceding paper.[3] The apparatus consists of a differentially pumped electron-impact ion source, a drift region 36 cm in length, and a differentially pumped quadrupole mass filter and electron multiplier. Rate coefficients have been determined using the additional residence time (ART) technique, which has been described in detail previously.[4] A pulse of parent ions is made to drift approximately halfway across the drift region by a uniform drift field $\vec{E}$, after which either the direction of the field is reversed or the field is turned off for a time Δt, and then the original field is restored. By varying the time Δt and measuring the loss of parent ions and/or the creation of product ions during the resulting additional residence time in the drift region, the reaction rate can be determined.

In the present studies the rate coefficients have, with one exception, been determined using the mode in which the drift field is turned off for a variable length of time, and therefore the ions are in thermal equilibrium with the neutral gas at the ambient temperature (300–306 K). In several cases the parent, rare-gas ions R^{2+} exist in several long-lived states exhibiting different mobilities.[3] By means of the ART technique, the reactivity of each of these groups of ions can be studied independently, as if only one group were present.

In order to obtain a large enough reactive loss of parent ions for accurate determinations of these slow charge-transfer rates, measurements have been made at high reactant concentrations (usually 0.1–1.3 Torr) and long ART intervals, 0.5–10 msec. A correction for lateral loss of ions due to diffusion must be applied to the data in order to extract the loss due to reaction. While the absolute value of the diffusion coefficient need not be known for this purpose, its change with the ions's mean energy must be obtained from a theoretical model. As in previous studies, Wannier's model for polarization scattering has been used.[5] Extensive studies with nonreacting ions were performed to test the validity of this model in several gases. The excellent agreement of the measurements with the model may be due in part to the fact that the values of E/N (N is the gas density) used during the drift phase of the measurements were kept as low as possible. Also, the rate coefficients have been measured under conditions where the diffusion correction is not very important.

Impurities contained in the rare-gas samples, as supplied, and background impurities introduced by the gas-handling system can be a potentially serious problem in measurements of very slow reactions. The ultrahigh-purity helium was further purified by a quartz diffusion cell, and liquid-nitrogen- or dry-ice-cooled cold traps (depending on the boiling point of the particular rare gas) were used at several points in the lines of the ultrahigh-vacuum gas-handling system. It was found that passage of the gases through liquid-nitrogen-cooled copper tubing removed some atmospheric gases quite effectively. Before and after each data run the mass spectrum of the ions emerging from the drift tube was scanned and, with the help of known ion-molecule rate coefficients, estimates were obtained of the impurity concentrations. Typically, less than 0.3 ppm of N_2 and a fairly constant pressure of H_2O of ~3×10^{-9} Torr were found. Krypton contained fairly large amounts of xenon (~20 ppm) and small amounts of hydrocarbons.

III. MEASUREMENTS

A. Reactions involving doubly charged ions

The charge-transfer reactions between rare-gas ions and atoms were found to occur as both two- and three-body reactions, i.e., the two processes

$$R_a^{2+} + R_b \to R_a^{+} + R_b^{+} \qquad (2)$$

and

$$R_a^{2+} + R_b + R_b \to R_a^{+} + R_b^{+} + R_b \qquad (3)$$

both contribute to the loss rate of R^{2+} ions. Denoting the two-body rate coefficient by k and the three-body coefficient by K, the effective two-body rate coefficient k_{eff} may be expressed in the form

$$k_{\mathrm{eff}} = k + K[R]. \qquad (4)$$

The coefficients k and K may then be obtained from the measured values of k_{eff} as a function of the rare-gas density $[R]$, as illustrated in Fig. 2.

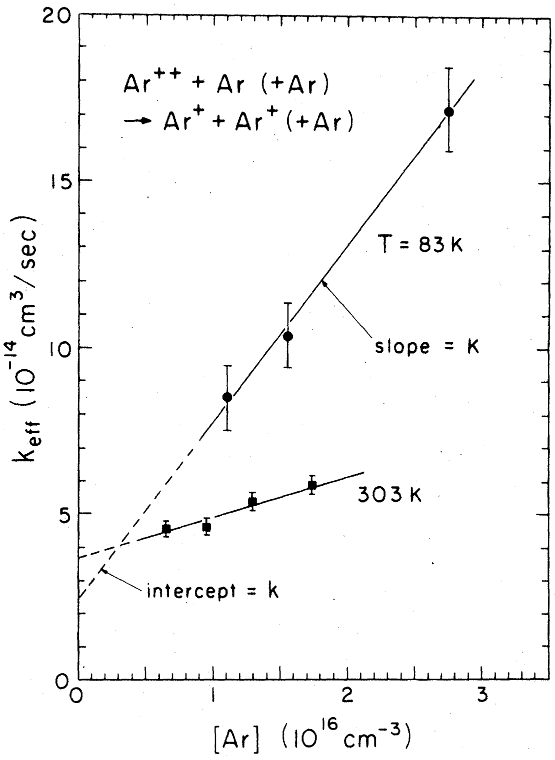

FIG. 2. Measured variation of the effective two-body rate coefficient with gas density at 83 and 303 K for Ar^{2+} ions in argon.

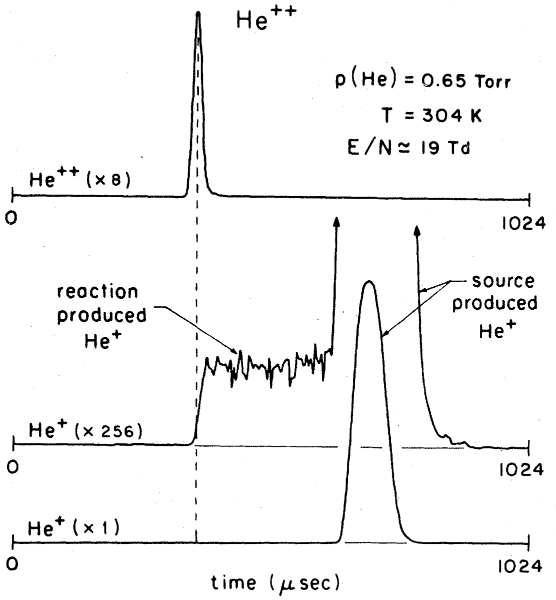

FIG. 3. Recorder tracings of the measured arrival time spectra of He^{2+} parent ions, of He^+ product ions resulting from the charge transfer reaction, and of He^+ ions which were produced in the ion source.

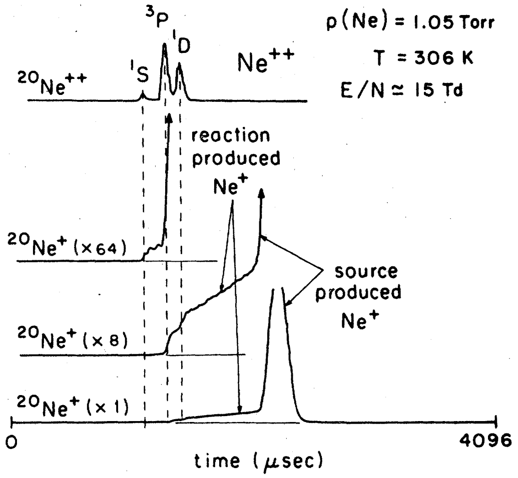

FIG. 4. Measured arrival time spectra of Ne^{2+} parent ions in three different states, of the Ne^+ ions produced by charge transfer involving each of these states, and of Ne^+ ions produced in the ion source.

Arrival-time spectra of the product ions were taken in order to determine whether the onset of the product ion arrival corresponded to the arrival time of the parent ions, as required if the product ion is formed from the parent ions. However, no quantitative determinations of the reaction rates were obtained from such data, the ART determinations being deemed more accurate. An example of such arrival time spectra is given in Fig. 3 for the case of He^{2+} ions producing He^+ ions. (Only the flat part of the He^+ arrival spectrum, extending from the arrival time of He^{2+} to that of He^+, is due to the charge-transfer reaction $He^{2+} + He$, the larger He^+ peak originating from He^+ ions produced in the ion source.)

A more complicated case is that of $Ne^{2+} + Ne$, shown in Fig. 4. Here, each of the three groups of Ne^{2+} ions belonging to the ^1S, ^3P, and ^1D states of Ne^{2+} (see preceding paper[3]) produces a Ne^+ product ion arrival spectrum. The superposition of all three contributions still shows quite clearly the small steps produced by the three groups of Ne^{2+} ions. Similar arrival time spectra were obtained in all cases where the parent ion R^{2+} reacts in its own gas. In the case of the reaction $Ne^{2+} + He$, however, only the product ion He^+ can be detected unambiguously. The Ne^+ ions have almost the same mobility as Ne^{2+} in helium; therefore, reaction-produced ions are obscured by the much larger signal from Ne^+ ions produced in the ion source.

1. $He^{2+} + He$

Data were taken at five different pressures between 0.35 and 1.1 Torr. The increase of the effective two-body rate coefficient with helium pressure over this range was only ~15%, leading to a poorly determined three-body rate coefficient, but an accurate value of the two-body coefficient A least-squares fit to the data (~30 data points) yielded the values $k = (4.8 \pm 0.5) \times 10^{-14}$ cm^3/sec and $K = (2.0 \pm 1) \times 10^{-31}$ cm^6/sec at 300 K. At ion mean energies corresponding to an effective temperature of ~1000 K, attained by maintaining appropriate E/N values during the ART measurements, the value $k = (1.0 \pm 0.2) \times 10^{-13}$ cm^3/sec was obtained.

The product ion He^+ was detected without difficulty, as indicated in Fig. 3. Estimates of the rate coefficient obtained from the intensity of the product ion relative to that of the parent ion agreed within about 50% with values obtained from the ART measurements of the He^{2+} loss rate. Better agreement was not expected, in view of complications in determining the absolute intensities of different ions.

There was no indication of a stable He_2^{2+} ion produced by the reaction $He^{2+} + 2He \rightarrow He_2^{2+} + He$. However, our ability to detect the doubly charged molecular ion, which should have a different mobility but the same mass-to-charge ratio as the singly-charged atomic ion, is not very good.

2. $Ne^{2+} + Ne$

As described in the preceding paper,[3] Ne^{2+} ions were observed in three states having differ-

TABLE I. Two- and three-body charge-transfer coefficients for doubly charged rare-gas ions in their parent gases at ~300 K (and also at 83 K for Ar^{2+} +Ar).

Reaction	Ionic state	K (10^{-14} cm^3/sec)	K (10^{-31} cm^6/sec)
He^{2+} +He	...	4.8 ± 0.5	2.0 ± 1
Ne^{2+} +Ne	^3P	2.1 ± 0.2	5.1 ± 1
	^1D	1.9 ± 0.2	3.5 ± 0.5
	^1S	2.7 ± 0.3	3.5 ± 0.5
Ar^{2+} +Ar	^3P	3.7 ± 0.4	13 ± 2
	^1D	~100	...
	^1S	600 ± 200	...
(T = 83 K)	(^3P)	(2.5 ± 1)	(54 ± 10)
Kr^{2+} +Kr	"A"	4.6 ± 0.5	22 ± 5
	"B"	~5	22 ± 5
Xe^{2+} +Xe	"A"	3.2 ± 0.3	27 ± 5
	"B"	...	...

ent mobilities. These were identified as the ^1S, ^3P, and ^1D states, in order of decreasing mobility. The rate coefficient for each state was determined separately over the pressure range 0.3–1.2 Torr. The measured rate coefficients, which are all near 2×10^{-14} cm^3/sec, are tabulated in Table I.

The Ne^+ product ions were observed clearly, as shown in Fig. 4. It is seen that all three states of Ne^{2+} contribute to the observed Ne^+ arrival spectrum. Since in the ART technique the reaction rate is determined from the measured loss of Ne^{2+} ions, it is necessary to consider to what extent deexciting collisions contribute to the loss of the excited Ne^{2+} ions. The observed shapes of the Ne^{2+} mobility peaks (see Fig. 3 of the preceding paper[3]) suggest that deexciting collisions are infrequent on the time scale of our measurements. For example, if a ^1S ion were transformed into a ^3P or a ^1D ion by a deexciting collision, it would continue its drift motion with a different mobility, leading to a contribution to the Ne^{2+} arrival time spectrum between the arrival peaks of the ions in the different states. Even at the highest pressures the arrival peaks remain clearly separated, and no contributions between peaks were noted. Furthermore, both the ^3P and the ^1D states of the Ne^{2+} ions exhibited the expected decay with ART, with no evidence of a source term resulting from quenching of excited states (i.e., ^1S into ^1D or ^3P; ^1D into ^3P).

A search was made for production of $Ne_2{}^{2+}$ ions, focusing on the molecular ion $(^{20}Ne\ ^{22}Ne)^{2+}$, since it would not be confused with either of the Ne^+ signals resulting from the two major neon isotopes. The reaction-produced signal observed at a mass-to-charge ratio of 21 amu was found to have about twice the amplitude expected for the $^{21}Ne^+$ isotope and almost exactly the same shape as the $^{20}Ne^+$ and $^{22}Ne^+$ signals. This observation, first thought to be an indication of production of stable Ne^{2+} ions, unfortunately may also result from the formation of a very small amount of $^{20}NeH^+$ contamination product, which cannot be excluded.

3. Ar^{2+} + Ar

Most experiments were carried out at argon pressures above ~0.2 Torr, where only a single mobility peak was observed. The Ar^{2+} ions are assumed to be in the ^3P ground state (see the discussion of the Ar^{2+} + He reaction for arguments supporting this conclusion). Since Ar^{2+} ions are readily produced in the ion source, the Ar^+ product ions were observed without difficulty, their arrival spectrum being stronger in intensity and similar in shape to that of He^+ produced by He^{2+} (see Fig. 3).

Measurements in argon were carried out at 300 and at 83 K. The latter measurements were made in a newly constructed, low-temperature drift-tube mass-spectrometer apparatus similar to one described earlier.[6] The results obtained at both temperatures are shown in Fig. 2. The dependence of k_{eff} on the argon density is seen to be considerably stronger at the lower temperature. The two-body rate coefficient at 83 K appears to be slightly smaller than that at 300 K, but the extrapolation to zero density is somewhat uncertain. The rate coefficients for this reaction are listed in Table I.

At low pressures (0.1 Torr at 300 K), a second group of Ar^{2+} ions of lower mobility was observed in argon. Their mobility peak partially overlapped the dominant ^3P peak, making it very difficult to obtain good rate coefficients for this group of Ar^{2+} ions. Estimates based on relative heights of the two mobility peaks gave a value $k \sim 1 \times 10^{-12}$ cm^3/sec for this group; however, we can not rule out the possibility that the loss of this ion group results from deexcitation as well as from charge transfer.

A third group of Ar^{2+} ions was observed when helium rather than argon was used as a buffer gas. Both of the Ar^{2+} states observed in argon buffer gas were found to react rapidly with helium; therefore this ion must be in a different state. Its reaction with argon was investigated by adding small amounts of argon (~0.01 Torr) to the helium (at ~0.5 Torr). The measured rate coefficient was found to be $(6 \pm 2) \times 10^{-12}$ cm³/sec.

The association of the different mobility groups of Ar^{2+} ions with specific states of the ion is somewhat difficult. We propose that the ions reacting slowly ($k \sim 4 \times 10^{-14}$ cm³/sec) with argon are ground state Ar^{2+} (^3P), the second group (having a lower mobility and $k \sim 10^{-12}$ cm³/sec) is the first excited state of Ar^{2+}, ^1D. This identification is in part based on the experimental observation of a higher appearance potential for the ion of lower mobility in argon and in part on the theoretical expectation that the excited states of Ar^{2+} have sufficient energy to react with argon via a faster, nearly resonant process of the type illustrated in Fig. 1(a) to produce excited Ar^{+*}, possibly ^2S. (For ground state Ar^{2+} ions this process is endoergic.) The Ar^{2+} ions observed in helium buffer gas might logically be expected to be in the next-higher excited state (^1S). We have used these somewhat tentative identifications of the various states in association with the reaction rates given in Table I.

4. $Kr^{2+} + Kr$

For Kr^{2+} ions in krypton, two ion groups having different mobilities were observed, and rate coefficients have been obtained for both types of ions. Although the association of the mobility peaks with particular states of the ion is not clear, the dependence of relative peak heights on the electron energy in the ions source suggests that the Kr^{2+} ion with the higher mobility belongs to an energetically higher state or states. The measured rate coefficients for the two Kr^{2+} ions, labeled "*A*" (higher mobility) and "*B*," are listed in Table I.

Since the krypton gas used was found to contain significant amounts (~20 ppm) of xenon, the sensitivity of the data to further addition of xenon was investigated. It appears that the ion with higher mobility reacts with xenon more rapidly than the ion with lower mobility. There was evidence, though, that only a portion of the ions in the higher mobility group took part in the reaction with xenon, suggesting the presence of different states of the Kr^{2+} ions.

5. $Xe^{2+} + Xe$

For Xe^{2+} ions in xenon, two ion groups with different mobilities were observed. Since the peak height of the lower mobility ion "*B*" was small (about 5%–10% of that of the higher-mobility ion), this ion group was not investigated systematically. However, its reactivity in xenon appeared comparable to that of the higher-mobility ion. Again the association of the mobility peaks with particular states of the ions is not clear. The measured rate coefficients are listed in Table I.

6. $Ne^{2+} + He$

Since the mobility of Ne^{2+} ions in helium does not depend on the state of the ions, we were unable to obtain rate coefficients for each of the ionic states. Studies in helium-neon mixtures indicated that none of the Ne^{2+} states reacts rapidly with helium; thus the measurements of the $Ne^{2+} + He$ rate coefficients are expected to refer to a mixture of all three states. Data were taken at helium pressures between 0.5 and 2 Torr. The two-body rate coefficient for this reaction was found to be quite small, $<10^{-14}$ cm³/sec (see Table II).

7. $Ar^{2+} + He$

The reaction of $Ar^{2+}(^1S)$ ions with helium appear to be very slow ($k < 10^{-14}$ cm³/sec). Unfortunately, several experimental problems, such as reaction of these ions with traces of argon reaching the

TABLE II. Two- and three-body charge-transfer coefficients for doubly and singly charged rare-gas ions in other rare gases at ~ 300 K. The notation $[-x]$ indicates 10^{-x}.

Reaction	Ionic state	K (cm³/sec)	K (cm⁶/sec)
$Ne^{2+} + He$	$^3P, ^1D, ^1S$ mixture	$(5.5 \pm 1)[-15]$	$(2.0 \pm 0.5)[-31]$
$Ar^{2+} + He$	^1S	$<[-14]$	
	^1D	$\sim 2[-10]$	...
	^3P	$(7 \pm 3)[-11]$	
$He^{+} + Ne$	^2S	$(1 \pm 0.5)[-15]$	...
$Ne^{+} + Ar$	^2P	$(6 \pm 1)[-15]$	$(5 \pm 2)[-32]$

drift region from the ion source and confusion of Ar^{2+} with Ne^{+} produced from the small amounts of neon impurity in the helium, precluded an accurate determination of this small rate coefficient.

By way of contrast, the ^{1}D and ^{3}P states of Ar^{2+} were found to react rapidly with helium when very small amounts ($\leq 10^{-3}$ Torr) were added to argon buffer gas (at ~0.1 Torr). The studies of these fast reactions will be described in a forthcoming paper; for completeness the measured rate coefficients are included in Table II.

B. Slow reactions involving singly charged ions He^{+} + Ne and Ne^{+} + Ar

While the primary effort in the present study was devoted to studies of reactions of doubly charged ions, the possibility that similar, slow charge-transfer reactions could be observed for singly charged ions was also investigated. The reaction $He^{+} + Ne$ was found to be too slow for a systematic study of the rate coefficient. At a helium pressure of 1.3 Torr, an effective two-body rate coefficient of order $\sim 1 \times 10^{-15}$ cm^3/sec was found, with an estimated uncertainty of about a factor of 2. Ne^{+} product ions were observed, leaving little doubt that the reaction occurs. Fairly good data were obtained for the reaction $Ne^{+} + Ar$. Both the two-body and three-body rate coefficients were found to be very small (see Table II). The product ion Ar^{+} was observed quite clearly.

IV. DISCUSSION

The mechanism responsible for the very slow charge-transfer reactions described in this paper is most probably radiative charge transfer. Although experimental confirmation would be provided by detection of the radiation emitted during the transfer process, the radiation is so weak and spread out in wavelength that our ongoing attempts to observe it are not likely to be successful.

One of the simplest reactions to analyze theoretically is $He^{2+} + He$, for which calculated potential curves are available.[7,8] As is seen in Fig. 5, the long range force between the incident He^{2+} ion and the He atom is slightly attractive, owing to the polarization induced in the atom. The short-range repulsion is slightly different for the states of u or g symmetry, but neither one intersects the repulsive curves of $He^{+} + He^{+}$ (the He_2^{2+} ground state) at energies accessible to thermal energy particles. Consequently, charge transfer is possible only through a radiative transition from the $^{1}\Sigma_u$ state.

Very recently, Cohen and Bardsley have carried out a semiclassical calculation of the rate coefficient for charge transfer between He^{2+} and He (see accompanying paper[7]). When they include an estimate of tunneling contributions to the charge transfer, they obtain the result $k(He^{2+}, He) \simeq 4.4 \times 10^{-14}$ cm^3/sec at 300 K, in excellent agreement with our result of $(4.8 \pm 0.5) \times 10^{-14}$ cm^3/sec. This new theoretical result represents a considerable improvement in accuracy over the pioneering calculation by Allison and Dalgarno,[9] where a rate coefficient of 4×10^{-15} cm^3/sec was obtained using less accurate wave functions for the He_2^{2+} states.

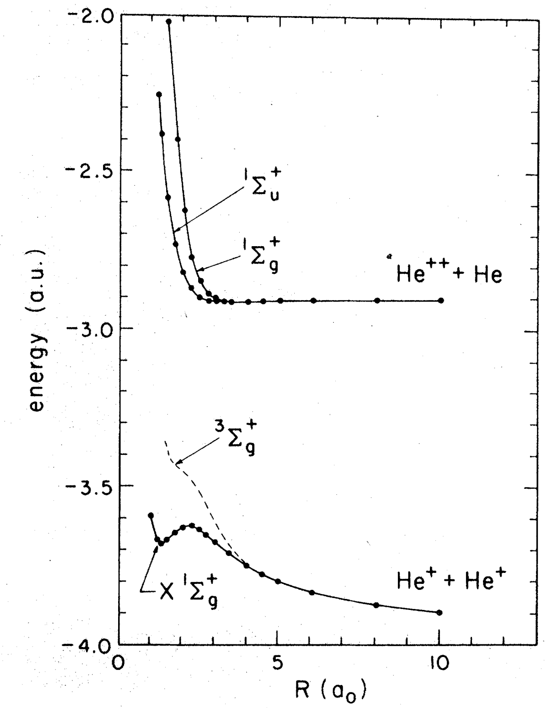

FIG. 5. Potential energy curves of the He_2^{2+} molecule calculated by Cohen and Bardsley (solid lines through the points) and by Browne (dashed line).

No charge-transfer rate coefficients have been calculated for the other rare-gas systems listed in Table I; however, systems of astrophysical interest, such as C^{2+} and C^{3+} colliding with H or N atoms, have been investigated by Butler *et al.*[10] The theoretical values of the single-electron charge-transfer coefficients are in the range 10^{-14}–10^{-13} cm^3/sec, rather close to the rate coefficients observed for the slow reactions of the various doubly charged rare-gas ions.

As noted in Sec. I, the three-body contribution to charge transfer in a system such as $He^{2+} + He$ is believed to involve formation of a weekly bound upper state of He_2^{2+} as a result of an energy-removing collision with a third body (He) as the He^{2+} and He collision partners near the classical turning point on the potential curve. This bound upper state subsequently radiates to the repulsive ground

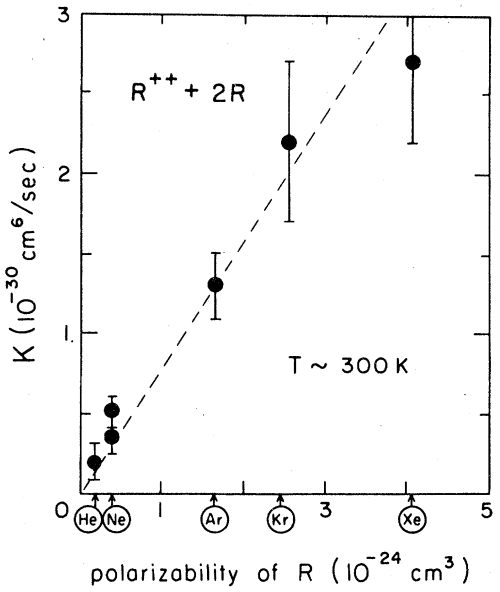

FIG. 6. Observed dependence of the three-body contribution to the charge-transfer reaction on the polarizability of the rare-gas atoms.

state, thus completing the charge-transfer reaction. The name "associative-radiative charge transfer" seems appropriate for this process.

As one might expect, the three-body process is observed to be more important in the heavier, more polarizable gases, and the rate coefficient increases with decreasing temperature, as evidenced by the $Ar^{2+} + 2Ar$ reaction. The general increase of the three-body coefficients with increasing polarizability of the atoms is shown in Fig. 6. It is not suggested, however, that the atomic polarizability is the only factor which determines the overall three-body rate coefficient.

Several of the reactions discussed in this paper have been studied in previous experiments at thermal energies and above. de Hoog and Oskam[11] investigated the decay of Ne^{2+} in neon afterglows and Ar^{2+} in argon afterglows by sampling the ions diffusing to the walls. Assuming two-body reaction kinetics in their analysis, they obtained rate coefficients of $k(Ne^{2+} + Ne) = 9 \times 10^{-14}$ cm³/sec and $k(Ar^{2+} + Ar) \leq 1.4 \times 10^{-13}$ cm³/sec, values about four times larger than those obtained in the present experiment. Neither contributions to ion loss by metastable states of the ions nor inclusion of the three-body process in the analysis of the afterglow experiments seems capable of removing the discrepancy; however, in view of the difficulties in obtaining quantitative determinations of slow reaction rates using the stationary afterglow technique, the disagreement may not be significant.

The finding by Howorka[12] of an even larger coefficient, $k(Ar^{2+} + Ar) = 4 \times 10^{-13}$ cm³/sec, from analysis of ions emerging from various regions of a hollow cathode discharge, in our opinion merely indicates the intrinsic difficulties of this method.

For the reaction of Ne^+ ions with krypton a very large thermal rate coefficient $k(Ne^+ + Kr) \sim 10^{-12}$ cm³/sec has been inferred from selected-ion drift-tube studies by Kaneko *et al.*[13] This rate is more than two orders of magnitude larger than we find; however, in the past this method has led to a serious overestimate of other slow reaction rates, perhaps due to the assumption in the analysis that the injected ion current is unchanged as the gas pressure in the drift tube is increased in order to increase reactive loss of the ions.

Although most of the charge-transfer processes described in this paper fall into the category of very slow reactions ($k < 10^{-13}$ cm³/sec), other noble-gas ion-atom systems exhibit much faster reaction rates, suggesting that quite different mechanisms are operative in the two cases. The $Ar^{2+} + Ar$ and $Ar^{2+} + He$ studies discussed in Sec. III serve to illustrate this point, since the different states of the Ar^{2+} ions exhibit reaction rates differing by orders of magnitude.

The differences in reactivity of the different ionic states may be made plausible with the aid of the energy level diagram of Fig. 7. For the $Ar^{2+} + Ar$ reaction, there are no slightly exoergic (by ~1 eV) channels available to $Ar^{2+}(^3P)$ ions; therefore the necessary curve crossings for the fast, nonradiative process illustrated in Fig. 1(a) do not exist.

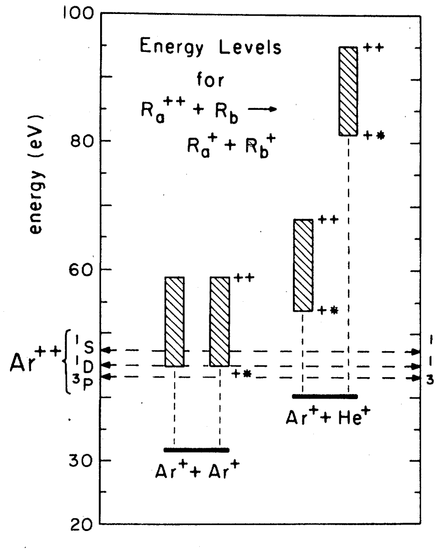

FIG. 7. Energies of the initial and final states of the system for charge transfer between Ar^{2+} ions and Ar or He atoms.

For the Ar^{2+} (^1D) and Ar^{2+} (^1S) states, production of Ar^{+*} ions in excited states leads to slightly exoergic channels (as suggested by the cross-hatched areas in Fig. 7); thus reaction rates of $\sim 10^{-12}$ to 10^{-11} cm^3/sec seem plausible. In the case of $Ar^{2+} + He$, the situation is less clear. The Ar^{2+} (^1S) + Ar state lies well above (~7 eV) the energy of the $Ar^+ + He^+$ product channel, and the reaction is slow ($k < 10^{-14}$ cm^3/sec), yet when the exoergicity of the reaction is reduced to ~5 eV and ~3 eV (for Ar^{2+} ions in the ^1D or ^3P states, respectively) the reaction becomes very fast ($\sim 10^{-10}$ cm^3/sec).

In general, a consideration of available final energy states for the various noble-gas ion-atom charge-transfer reactions indicates that fast reactions do occur in systems where slightly exoergic channels are available, so that appropriate curve crossings between initial and final states occur. The results of these studies of fast charge transfer reactions will be the subject of a forthcoming paper.

Radiative charge-transfer processes may play important roles in certain laser plasmas, fusion plasmas, and interstellar clouds. Thus our ability to measure rate coefficients for these slow reactions in the laboratory provides a means for obtaining needed data for modeling these environments and for comparison with theoretical calculations.

ACKNOWLEDGMENT

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

---

[1] R. Johnsen, M. T. Leu, and M. A. Biondi, Phys. Rev. A 8, 1808 (1973).

[2] E. Graham, M. A. Biondi, and R. Johnsen, Phys. Rev. A 13, 965 (1976).

[3] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 989 (1978), preceding paper.

[4] J. Heimerl, R. Johnsen, and M. A. Biondi, J. Chem. Phys. 51, 5041 (1969).

[5] See, for example, E. W. McDaniel and E. A. Mason, *The Mobility and Diffusion of Ions in Gases* (Wiley, New York, 1973).

[6] R. Johnsen, C. M. Huang, and M. A. Biondi, J. Chem. Phys. 63, 3374 (1975).

[7] J. S. Cohen and J. N. Bardsley, Phys. Rev. A 18, 1004 (1978), accompanying paper.

[8] J. C. Browne, J. Chem. Phys. 42, 1428 (1965).

[9] D. C. S. Allison and A. Dalgarno, Proc. Phys. Soc. Lond. 85, 845 (1965).

[10] S. E. Butler, S. L. Guberman and A. Dalgarno, Phys. Rev. A 16, 500 (1977).

[11] F. J. de Hoog and H. J. Oskam, J. Appl. Phys. 44, 3496 (1973).

[12] F. Howorka, J. Chem. Phys. 67, 2919 (1977).

[13] Y. Kaneko, M. Namiki, and N. Kobayashi, Abstracts of the Tenth International Conference on the Physics of Electron and Atomic Collisions, Paris, 1977 (unpublished).