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Thermal-energy charge transfer, quenching, and association reactions of doubly charged ions in the rare gases

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A drift-tube mass-spectrometer apparatus has been used to determine thermal-energy (300 K) charge transfer rate coefficients for reactions of the type $R_a{}^{2+} + R_b \rightarrow R_a^{+} + R_b^{+*}$ and $R_a{}^{2+} + R_b \rightarrow R_a^{+} + R_b{}^{2+} + e^{-}$ (transfer ionization), where R = He, Ne, Ar, Kr, and Xe. Rate coefficients for ions in the low-lying, metastable excited states (^1S and ^1D) as well as the ground state (^3P) have been determined and, in some cases, deexcitation (quenching) coefficients for ^1S and ^1D ions have been measured. Reactions with an exoergicity $\Delta E \sim 4$ eV are found to be fast, approaching the limiting Langevin rate, while for $\Delta E < 2$ and >7 eV the rates fall off dramatically, in some cases dropping to the radiative value ($\sim 10^{-14}$ cm^3/sec). The equilibrium constant for the three-body association reaction $\mathrm{Xe}^{2+} + 2\,\mathrm{Ne} \rightleftharpoons (\mathrm{Xe\,Ne})^{2+} + \mathrm{Ne}$ has been determined at 300 K.

I. INTRODUCTION

In two recent publications we described measurements of the ionic mobilities[1] and the very slow, single-electron radiative charge-transfer reactions[2] of doubly charged rare-gas ions in their parent gases. In the course of that investigation and in subsequent work the majority of the reactions occurring between doubly charged ions and atoms belonging to different rare-gas species have also been studied. A fairly complete set of rate coefficients for ion-atom combinations of the five common rare gases has been obtained, including reaction processes involving the low-lying metastable states of the doubly charged ions.

In many cases fast, single-electron charge transfer is found to proceed via the reaction path

$$X^{2+} + Y \rightarrow X^{+} + Y^{+*}, \tag{1}$$

in which one of the product ions is left in an excited state (denoted by the asterisk). Also, when energetically allowed, the single-electron transfer may leave the reactant atom in a continuum state corresponding to a doubly charged ion plus free electron,

$$X^{2+} + Y \rightarrow X^{+} + Y^{2+} + e^{-}. \tag{2}$$

This process is sometimes referred to as transfer ionization.[3]

The low-lying metastable states of the doubly charged ions have been observed to be deexcited (quenched) in several cases, and the quenching rate coefficients have been determined for a number of these reactions.

Finally, three-body association of a doubly charged ion with a rare-gas atom has been observed to occur in the reaction

$$\mathrm{Xe}^{2+} + 2\mathrm{Ne} \rightleftharpoons (\mathrm{XeNe})^{2+} + \mathrm{Ne}, \tag{3}$$

and an estimate for the equilibrium constant has been obtained at 300 K for this reaction.

No clear evidence for the nonresonant process of asymmetric, two-electron transfer has been found in the systems that have been studied. While the resonant process of symmetric, two-electron transfer probably occurs between doubly charged ions and their parent atoms,[4] in our apparatus this is not detectable as a "reaction"; rather such charge transfer would affect the ionic mobility in the parent gas.[1]

In the following we will briefly describe experimental procedures used, present the results of experimental measurements, and discuss our results in terms of potential-curve-crossing models.

II. EXPERIMENTAL METHOD AND APPARATUS

For the present studies the same drift-tube mass-spectrometer apparatus and associated techniques were used as in the previous measurements of slow reactions of doubly charged ions.[1,2] The apparatus consists of an electron-bombardment ion source from which ions were injected across a differentially pumped region into a long (36.2-cm), uniform-field drift region containing a buffer gas with small additions of reactant gas. Ions exiting a small aperture at the end of the drift region entered a differentially pumped quadrupole mass spectrometer for identification and ion counting. By using the ions' parent gas as the buffer with small additions of the reactant (generally less than 0.1%), ions in their ground and excited states are distinguishable as a result of their different mobilities and thus can be studied independently. In cases where different states of the ion have the same mobility, other methods such as selective destruction or quenching of one state have to be used to distinguish between reactions of different excited states. (These techniques will be described in more detail in the sections on particular reactions.)

The additional-residence-time technique (ART) was used[5] to determine the reaction rates at thermal energy (i.e., the electric drift field was turned off during the additional residence time). Rate coefficients were obtained from measurements of the parent ions' loss rate in the presence of the reactant gas (with corrections for losses occurring through reactions with the buffer gas and through lateral diffusion, as determined in separate experiments). In several cases it was found advantageous to obtain rate coefficients by an alternative scheme, i.e., from measurements of the product-ion arrival spectrum,[5] in which case the necessity of maintaining a small drift field means that the rate coefficients refer to ion energies slightly above thermal. The analysis of the product-ion arrival spectrum to yield the rate coefficient was carried out in a manner similar to the procedure described by Heimerl *et al.*,[5] with a slight modification for the fact that the Einstein relation, $D/\mu = kT/Ze$, relating the diffusion coefficient D and mobility μ of the ions depends on the charge of the ion, Ze.

The observation of the desired reaction-product ions may often be complicated (a) by extraneous reactions of the numerous singly charged ions from the source which enter the drift region along with the doubly charged parent ions under study, (b) by reaction products resulting from slow reactions of parent ions with the buffer gas, and (c) by secondary reactions of the product ions with the buffer gas. A variety of methods have been used in such cases to verify that the production of singly or doubly charged product ions results from the parent ions under study. Differences in ionic mobility of doubly and singly charged ions, the variation of observed reaction products with presence or absence of parent ions and with the presence or absence of the reactant gas can be used to separate contributions from different reactions.

Secondary reactions of the product ions with the buffer gas occur mainly in cases where the reaction product is a doubly charged ion. While use of a different ("nonparent") buffer gas can often eliminate the undesired secondary reactions, the loss of mobility-differentiation among the various excited states of the parent ion means that it is generally no longer possible to separate contributions to the product-ion formation resulting from the different excited states. (Some of the complications encountered are discussed in more detail in the sections on particular reactions.)

Estimates or upper limits for some slow reactions (having rate coefficients of less than 10^{-13} cm^3/sec) were obtained by observing the decay of the parent ion in pure reactant gas. No attempt was made to determine these small rate coefficients accurately; also, possible three-body contributions to these rate coefficients have not been investigated in detail.

Typical gas pressures employed for the measurements ranged from about 0.1 Torr to about 1 Torr, depending on the particular gas under study. In general, the heavier rare gases krypton and xenon were used at low pressures (0.1 to 0.3 Torr), the lighter rare gases at higher pressures (0.3 to 1.0 Torr). Impurities contained in the gas samples are usually less important in measurements of fast reaction processes; nevertheless the same gas-handling procedures found desirable for the more difficult measurements of very slow reactions[2] were followed. However, helium, as supplied, was found to be sufficiently pure for the measurements.

Except as noted, the uncertainties in the measured rate coefficients are not expected to exceed ±20% and in many cases are probably substantially smaller. The largest single source of error arises from uncertainties in the determinations of the small reactant gas pressures (5×10^{-5} to 10^{-3} Torr). Such determinations are subject to complications in differentially pumped drift tubes.[5]

III. RESULTS

The measurement of the parent ions' loss rate which yields the reaction rate coefficient is a rather straightforward procedure and thus will not be discussed in detail. The measured rate coefficients and observed reaction channels at 300 K have been compiled in Tables I–V, together with the results of the earlier work on slow reactions of doubly charged ions with their parent gases.[2] In the tables, a question mark indicates some doubt that the reaction branch occurs. Where a number of excited product states are possible, several relevant energy defects ΔE are given; where many exist, dots are used. (For more detail, the reader is referred to standard references on atomic energy levels.) The last column of the tables gives the ratio of the measured coefficient k to the limiting Langevin rate coefficient k_L.

A. Reactions of He^{2+} ions

Except for the reaction with helium discussed previously,[2] all reactions of He^{2+} ions with rare-gas atoms are found to be fast, approaching the limiting Langevin rate (see Table I). For the reactions in krypton and xenon the doubly charged

TABLE I. Reactions of He^{2+} ions. The notation $(-x)$ corresponds to 10^{-x}. Only ΔE's of significance for the reactions are listed. The last column gives the ratio of the measured rate coefficient k to the limiting Langevin rate coefficient k_L.

Reaction	k (cm^3/sec)	ΔE (eV)[a]	k/k_L
$He^{2+} + He \rightarrow He^+ + He^+$	4.8 ± 0.5 (−14)[b]	29.8	3.25 (−5)
$He^{2+} + Ne \rightarrow He^+ + Ne^+$	8.4 ± 2.0 (−10)	6, 5.7, 2.4	0.52
$He^{2+} + Ar \rightarrow He^+ + Ar^{2+} + e^-$	2.6 ± 0.5 (−9)	Continuum	0.83
$\rightarrow He^+ + Ar^+$ (?)		>11	
$He^{2+} + Kr \rightarrow He^+ + Kr^{2+} + e^-$	3.9 ± 0.6 (−9)	Continuum	0.97
$\rightarrow He^+ + Kr^+$ (<20%)		>15.8	
$He^{2+} + Xe \rightarrow He^+ + Xe^{2+} + e^-$	4.7 ± 0.7 (−9)	Continuum	0.98
$\rightarrow He^+ + Xe^+$ (<20%)		1.5, >21	

[a] Calculated from data in C. E. Moore, *Atomic Energy Levels*, U. S. Natl. Bur. Stand. Circ. No. 467 (U. S. GPO, Washington, D. C., 1958).

[b] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978).

ions Kr^{2+} and Xe^{2+}, respectively, are the only positively identified reaction products. The possibility that other, less probable reaction branches produce Kr^+ and Xe^+ ions cannot be excluded completely; however these branches are estimated to contribute not more than ~20% to the total reaction rate.

Since He^+ ions are also observed to be a product of the reactions of He^{2+} ions with krypton and xenon, it appears very unlikely that two-electron transfer is the mechanism responsible but instead that the reaction occurs through the "transfer ionization" process alluded to in reaction (2), i.e.,

$$He^{2+} + Kr \rightarrow He^+ + Kr^{2+} + e^- \tag{4}$$

and

$$He^{2+} + Xe \rightarrow He^+ + Xe^{2+} + e^- , \tag{5}$$

with the product electron remaining undetected. Attempts to detect these electrons indirectly through the impact ionization which should result when such electrons traverse the drift tube in a direction opposite to the positive ions did not yield conclusive results. Some ionization was observed, but the possibility of other effects giving rise to the ionization (e.g., uv photons from the ion source or release of electrons from surfaces struck by ions) could not be excluded. Finally, the extremely large rate coefficients observed for these processes also suggest that one- rather than two-electron transfer is the reaction occurring.

Only singly charged ions are observed in studies of the reaction $He^{2+} + Ar$, even though transfer ionization in argon is energetically possible. It is likely that Ar^{2+} ions are produced in the reaction but are not detected because they undergo a fast secondary reaction with the helium buffer gas to produce singly charged Ar^+ ions. As no other buffer gas is suitable for the study of the He^{2+}-ion reactions, this hypothesis could not be tested.

The reaction $He^{2+} + Ne$ is found to be fast, producing only singly charged Ne^+ ions. In contrast to the argon case just discussed, Ne^{2+} ions should be detected, if formed, since these ions do not react rapidly with helium. However, in neon transfer ionization is not energetically possible, and evidently the two-electron transfer process is too slow to yield a detectable Ne^{2+} signal.

B. Reactions of Ne^{2+} ions

As reported earlier,[1] three different groups of Ne^{2+} ions are distinguishable as a result of their different mobilities in neon. These groups have been identified as ions in the ^1S state (highest mobility), $^3P_{2,1,0}$ states (intermediate mobility), and ^1D state (lowest mobility). In the present studies further measurements of the appearance potentials of these ionic groups have been made which support this identification.

The slow reactions of Ne^{2+} with helium and neon have been described earlier.[2] The reactions with argon, krypton, and xenon are found to have large rate coefficients, approaching the Langevin limit (see Table II). For all three states of Ne^{2+} (^1S, ^1D, and ^3P) transfer ionization is energetically possible in krypton and xenon; however in argon the process is endoergic for Ne^{2+} (^3P) ions.

The detection of doubly charged product Ar^{2+} ions from the reaction of Ne^{2+} with argon is seriously complicated (a) by the secondary reaction of Ar^{2+} ions with the neon buffer gas (see Sec. III C) and (b) by mass-spectrometric coincidence of Ar^{2+} and Ne^+ ions. Measurements in helium buffer suf-

TABLE II. Reactions of Ne^{2+} ions. Same format as Table I.

State	Reaction	k ($\mathrm{cm}^3/\mathrm{sec}$)	ΔE (eV)	k/k_L
^3P	$\mathrm{Ne}^{2+} + \mathrm{He} \rightarrow \mathrm{Ne}^{+} + \mathrm{He}^{+}$	5.5 ± 1 (−15) [a]	16.5	4.7 (−6)
^1D			19.7	
^1S			23.4	
^3P	$\mathrm{Ne}^{2+} + \mathrm{Ne} \rightarrow \mathrm{Ne}^{+} + \mathrm{Ne}^{+}$	2.1 ± 0.2 (−14) [a]	19.7	2.3 (−6)
^1D		1.9 ± 0.2 (−14) [a]	22.7	2.0 (−5)
^1S		2.7 ± 0.3 (−14) [a]	26.4	2.9 (−5)
^3P	$\mathrm{Ne}^{2+} + \mathrm{Ar} \rightarrow \mathrm{Ne}^{+} + \mathrm{Ar}^{+}$	5.3 ± 1 (−10)	0.5, . . . , 6.0	0.32
^1D	$\mathrm{Ne}^{2+} + \mathrm{Ar} \rightarrow \mathrm{Ne}^{+} + \mathrm{Ar}^{+}$ $\rightarrow \mathrm{Ne}^{+} + \mathrm{Ar}^{2+} + e^{-}$	7.0 ± 1 (−10)	0.9, . . . , 6.0 Continuum	0.43
^1S	$\mathrm{Ne}^{2+} + \mathrm{Ar} \rightarrow \mathrm{Ne}^{+} + \mathrm{Ar}^{+}$ $\rightarrow \mathrm{Ne}^{+} + \mathrm{Ar}^{2+} + e^{-}$	1.0 ± 0.3 (−9)	4.6, . . . Continuum	0.61
^3P	$\mathrm{Ne}^{2+} + \mathrm{Kr} \rightarrow \mathrm{Ne}^{+} + \mathrm{Kr}^{+}$ $\rightarrow \mathrm{Ne}^{+} + \mathrm{Kr}^{2+} + e^{-}$	1.7 ± 0.3 (−9)	2.5, . . . , 6.0	0.93
^1D		8.0 ± 2 (−10)	5.7, . . . Continuum	0.44
^1S		1.7 ± 0.3 (−9)	9.4, . . .	0.93
^3P	$\mathrm{Ne}^{2+} + \mathrm{Xe} \rightarrow \mathrm{Ne}^{+} + \mathrm{Xe}^{+}$ $\rightarrow \mathrm{Ne}^{+} + \mathrm{Xe}^{2+} + e^{-}$	1.9 ± 0.3 (−9)	5.7, . . . Continuum	0.84
^1D	$\mathrm{Ne}^{2+} + \mathrm{Xe} \rightarrow \mathrm{Ne}^{+} + \mathrm{Xe}^{2+} + e^{-}$	1.6 ± 0.3 (−9)	Continuum	0.71
^1S	$\mathrm{Ne}^{2+} + \mathrm{Xe} \rightarrow \mathrm{Ne}^{+} + \mathrm{Xe}^{2+} + e^{-}$	2.0 ± 0.4 (−9)	Continuum	0.89

[a] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978).

fer from the reaction of Ar^{2+} with helium. Consequently, we are unable to determine the primary product ions of the $\mathrm{Ne}^{2+}+\mathrm{Ar}$ reaction.

For the reaction $\mathrm{Ne}^{2+}+\mathrm{Kr}$ the Kr^{2+} ion is not observable as a product in neon buffer gas because of the secondary reaction of Kr^{2+} with neon (see later discussion of Kr^{2+} reactions); however, in helium buffer it is readily detected. Unfortunately it is not possible to distinguish contributions to the observed Kr^{2+} signal from the different states of Ne^{2+}, since their mobilities in helium do not differ sufficiently to provide separation in the arrival spectra of the product ions.

Products from the reaction of Ne^{2+} with xenon are detected quite clearly, and it is found that while the ^1D and ^1S states produce Xe^{2+} ions exclusively, the ^3P state produces both Xe^{+} and Xe^{2+} ions with nearly equal probability. [The possibility that the Xe^{+} and Xe^{2+} ions produced by the $\mathrm{Ne}^{2+}(^3P)$ ions originate from different sublevels of the ^3P state could not be tested experimentally.] Since Ne^{+} ions were also observed as products, there is little doubt that transfer ionization, rather than two-electron transfer, is the dominant reaction mechanism.

C. Reactions of Ar^{2+} ions

As discussed previously,[2] only one of the Ar^{2+} states, identified as ^3P, reacts with argon sufficiently slowly to transit the drift tube and thus remains detectable at argon pressures above 0.1 Torr. A second state of Ar^{2+}, tentatively identified as ^1D, is observable at low argon pressures (<0.1 Torr). The mobility of $\mathrm{Ar}^{2+}(^1D)$ ions is only slightly less than that of $\mathrm{Ar}^{2+}(^3P)$ ions, making it very difficult to separate effects of the two states; consequently all rate coefficients given for $\mathrm{Ar}^{2+}(^1D)$ ions are rough estimates. Also, the possibility that deexcitation (quenching) reactions contribute to the loss of the ^1D ions cannot be excluded. A third group, probably consisting solely of $\mathrm{Ar}^{2+}(^1S)$ ions, is observable in helium buffer gas. While the intensity of this ion in helium is generally quite small, confusion with Ne^{+} (which has the same charge-to-mass ratio) can be avoided by making use of their differing mobilities and reactivities.

No doubly charged product ions were observed to arise from any of the Ar^{2+} reactions. Also, no clear evidence of quenching (deexcitation) of

TABLE III. Reactions of Ar^{2+} ions. Same format as Table I.

State	Reaction	k (cm^3/sec)	ΔE (eV)	k/k_L
^3P		7 ±2 (−11)	3.0	6.4 (−2)
^1D	$Ar^{2+} + He \rightarrow Ar^+ + He^+$	~1.4 (−10)	4.8	~0.13
^1S		≲2 (−14)	7.0	1.8 (−5)
^3P		3.7 ± 0.7 (−12)	6.1	4.6 (−3)
^1D	$Ar^{2+} + Ne \rightarrow Ar^+ + Ne^+$	<3.7 (−12)	7.8	<4.6 (−3)
^1S		<1 (−13)	10.0	<1.3 (−4)
^3P		3.7 ± 0.4 (−14) [a]	11.9	2.8 (−5)
^1D	$Ar^{2+} + Ar \rightarrow Ar^+ + Ar^+$	4^{+3}_{-2} (−13) [a]	0.1, 13.6	3 (−4)
^1S		6.3 ± 1 (−12) [a]	2.4	4.7 (−3)
^3P		≲2 (−13)	0.1, 13.6	≲1.4 (−4)
^1D	$Ar^{2+} + Kr \rightarrow Ar^+ + Kr^+$	≲2 (−13)	0.9, 1.9	≲1.4 (−4)
^1S		1.4 ± 0.3 (−9)	3.1, 4.1	1.0
^3P		1.5 ± 0.3 (−9)	4.2, . . .	0.88
^1D	$Ar^{2+} + Xe \rightarrow Ar^+ + Xe^+$	~1.5 (−9)	3.7, . . .	~0.88
^1S		1.0 ± 0.2 (−9)	~0, . . . , 8.2	0.6

[a] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978).

$Ar^{2+}(^1S)$ was found; however, since the lower states of Ar^{2+} react rapidly with the helium buffer gas, these deexcitation products are unobservable. The rate coefficient for the $Ar^{2+}(^3P)$+Ne reaction was determined from the arrival spectrum of $^{22}Ne^+$, thus avoiding the difficulty of distinguishing Ar^{2+} from $^{20}Ne^+$ ions in the mass spectrometer. Only reactions of Ar^{2+} ions with krypton and xenon approach the limiting Langevin rate (see Table III).

D. Reactions of Kr^{2+} ions

As noted in our earlier studies,[1] two groups of Kr^{2+} ions can be distinguished by their different mobilities in krypton, groups A (higher mobility) and B (lower mobility). The association of the two groups with the appropriate excited states of Kr^{2+} was not clear; however the appearance-potential measurements suggested that group-A ions consisted of Kr^{2+} ions in excited state(s).

A fast reaction of Kr^{2+} ions with xenon is found to occur for a portion (~40%) of the ions contained in group A (subgroup A_1). It was noted that the reaction of A_1-type ions with xenon did not take place when small amounts (less than 1%) of helium were added to the krypton. Since no charge transfer of Kr^{2+} ions with helium is detected, the $Kr^{2+}(A_1)$ ions are evidently quenched by helium to another state A_2 in the A group (the sum of A_1 and A_2 ions remained unaffected by the addition of helium). A lower limit for the quenching rate coefficient of $Kr^{2+}(A_1)$ with helium of $k_q \geq 10^{-11}$ cm^3/sec was obtained from the measured helium density and the residence time of Kr^{2+} ions in the drift tube.

Studies of the reaction of Kr^{2+} ions with neon also showed that $Kr^{2+}(A\ )$ ions react with two different rate coefficients. The reaction of $Kr^{2+}(A_2)$ ions with neon was studied either by destroying the A_1 state ions in the reaction with xenon or by deexciting A_1 to A_2 ions by addition of small amounts of helium to the krypton buffer gas. Both types of measurements yielded the same rate coefficient for $Kr^{2+}(A_2)$+Ne. The reaction of Kr^{2+} ions with neon was then studied for the remaining states of Kr^{2+} by adding larger amounts of neon to krypton (without adding either xenon or helium), so that the fastest reacting state (A_2) was preferentially destroyed. It was found that the remaining states of Kr^{2+} react with neon with rate coefficients of the order of 10^{-10} cm^3/sec. The observation that the rate coefficient for $Kr^{2+}(B)$ ions showed some variation with neon pressure indicates the presence of at least two different states in the B group; however, no reaction was found which clearly distinguished the different excited-state components of $Kr^{2+}(B)$ ions.

No reaction of Kr^{2+} ions with argon was found to occur with rate coefficients in excess of 10^{-13}

TABLE IV. Reactions of Kr^{2+} ions. Same format as Table I.

State	Reaction	k (cm^3/sec)	ΔE (eV)	k/k_L
Charge transfer				
$A, B(^3P, ^1D)$	$Kr^{2+} + He \rightarrow Kr^+ + He^+$	<1 (−14)	−0.02, 1.8, 4.1	<9.5 (−6)
$A_1(^1S)$	$Kr^{2+} + Ne \rightarrow Kr^+ + Ne^+$	1.3 ± 0.3 (−10)	6.5, 7.1	0.18
$A_2(^1D)$		5 ± 2 (−10)	4.8	0.8
$B(^3P_{2,1,0})$		0.6–1.3 (−10)	3.0, 3.6, 3.7	0.17
$A, B(^3P, ^1D, ^1S)$	$Kr^{2+} + Ar \rightarrow Kr^+ + Ar^+$	$\lesssim 1$ (−13)	8.8, 10.6, 12.9	<8.7 (−5)
$A(^1D, ^1S)$	$Kr^{2+} + Kr \rightarrow Kr^+ + Kr^+$	4.6 ± 0.5 (−14) [a]	1.4, 12.4	4 (−5)
$B(^3P)$		5.0 ± 0.5 (−14) [a]	10.6	4.4 (−5)
$A_1(^1S)$	$Kr^{2+} + Xe \rightarrow Kr^+ + Xe^+$	1.2 ± 0.6 (−11)	3.0, 5.2	9.1 (−3)
$A_2, B(^1D, ^3P)$		<1 (−13)	0.7, 1.0, 3.0	<7.6 (−5)
Deexcitation (quenching)				
$A_1(^1S)$	$Kr^{2+}(A_1) + He \rightarrow Kr^{2+}(A_2) + He$	$>10^{-11}$		

[a] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978).

cm^3/sec. Deexcitation of excited Kr^{2+} states by argon has not been investigated in detail; however, none seems to occur between states having different mobilities.

Some tentative conclusions can be drawn concerning the identity of the observed groups of Kr^{2+} ions. The appearance-potential measurements indicate that both the A_1 and A_2 groups belong to excited states of Kr^{2+}, and the observed quenching indicates that A_1 is energetically higher than A_2. This finding suggests that A_1 contains ions in the ^1S state, A_2 the ^1D state, and the B group the ^3P state. The slight variations in reactivity of $Kr^{2+}(B)$ ions may be due to the $J = 2, 1, 0$ sublevels of the ^3P state, possibly with $^3P_2$ (lowest state) reacting differently than $^3P_1$ and $^3P_0$. This suggested identification of the Kr^{2+} states has been included in Table IV.

E. Reactions of Xe^{2+} ions

Two groups of Xe^{2+} ions have been distinguished by their differing mobilities[1] in xenon, the A group (higher mobility, ~92% of the Xe^{2+} ions) and the B group (lower mobility, ~8% of the Xe^{2+} ions). Appearance-potential measurements indicate that $Xe^{2+}(B)$ ions belong to an excited state of the ion. A further splitting of the $Xe^{2+}(A)$ ions into subgroups A_1, A_2, and A_3 became apparent in measurements of the Xe^{2+}-ion reactions with helium, neon, and argon. The results of the studies are summarized in Table V.

The group A_1 (17% of all Xe^{2+} ions) did not take part either in charge transfer or in quenching reactions with helium, neon or argon. The group A_2 (25% of all Xe^{2+} ions) was found to be quenched to the $Xe^{2+}(B)$ state by both helium and neon. The group A_3 (50% of all Xe^{2+} ions) was observed to undergo a fast charge transfer reaction with argon. Rate coefficients for the quenching reactions were obtained from the arrival spectrum of $Xe^{2+}(B)$ ions, which appears as a small contribution between the transit times of the $Xe^{2+}(A)$ and $Xe^{2+}(B)$ ions. For charge transfer in argon the rate coefficient was inferred from the arrival spectrum of the Ar^+ product ions.

A tentative identification of the states associated with the various groups of Xe^{2+} ions which best fits the observations is given in Table V. The quenching reactions show that the group A_2 corresponds to an energetically higher state than does group B which, according to appearance-potential measurements, also corresponds to an excited state. This finding suggests that A_2 contains ions in the ^1S state and that B contains ions in the ^1D state. Consequently the groups A_1 and A_3 should be associated with different sublevels of the ^3P state, perhaps the $^3P_2$ ground-state and the $^3P_{0,1}$ states. (The energy difference between $^3P_2$ and $^3P_0$ is ~1.0 eV, compared with a difference of 0.21 eV between $^3P_0$ and $^3P_1$). It appears likely that the A_3 state reacting with argon is $^3P_2$ rather than $^3P_{0,1}$ (see discussion of Xe^{2+} reactions in Sec. IV).

Since charge transfer of $Xe^{2+}(^3P_2)$ ions with neon is not energetically possible, formation of stable

TABLE V. Reactions of Xe^{2+} ions. Same format as Table I.

State	Reaction	k (cm^3/sec)	ΔE (eV)	k/k_L
Charge transfer				
$A_3(^3P_2)$ $A_1(^3P_{0,1})$ $B(^1D)$	$Xe^{2+} + Ne \rightarrow Xe^+ + Ne^+$	<1 (−14)	<1.8	<1.4 (−5)
$A_3(^3P_2)$	$Xe^{2+} + Ar \rightarrow Xe^+ + Ar^+$	3.9 ± 0.4 (−10)	4.1, 5.4	0.36
$A_1(^3P_{0,1})$ $A_2(^1S)$ $B(^1D)$	$Xe^{2+} + Ar \rightarrow Xe^+ + Ar^+$	<2 (−14)	6.4, ...	<1.9 (−5)
$A(^3P, ^1S)$ $B(^1D)$	$Xe^{2+} + Kr \rightarrow Xe^+ + Kr^+$	<8 (−14)	0.4, >7.2	<7.8 (−5)
$A(^3P, ^1S)$	$Xe^{2+} + Xe \rightarrow Xe^+ + Xe^+$	3.3 ± 0.4 (−14) [a]	9.1, ..., 2.4	2.8 (−5)
$B(^1D)$	$Xe^{2+} + Xe \rightarrow Xe^+ + Xe^+$	~3 (−14) [a]	11.2, ...	2.6 (−5)
Deexcitation (quenching)				
$A_2(^1S)$	$Xe^{2+} + He \rightarrow Xe^{2+}(B) + He$	$\sim 10^{-10}$	2.5	9.3 (−2)
$A_2(^1S)$	$Xe^{2+} + Ne \rightarrow Xe^{2+}(B) + He$	1.1 ± 0.4 (−10)	2.5	0.16

[a] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978).

$(XeNe)^{2+}$ by a three-body association process, reaction (3), may occur. Experiments carried out by injecting Xe^{2+} ions into neon (at 0.3 to 1.0 Torr) showed that at room temperature (300 K) a reaction equilibrium exists between these atomic and molecular doubly charged ions, with an equilibrium constant $K \equiv k_+/k_- \simeq 1.5 \times 10^{-19}$ cm^3. The concentration of $(XeNe)^{2+}$ at 1 Torr of neon was about 0.5% of Xe^{2+} and varied linearly with density as the neon pressure was decreased, as expected for an equilibrium process. The observation that the apparent mobility of $(XeNe)^{2+}$ corresponds exactly to that of Xe^{2+} in neon is further evidence of an equilibrium (rapid formation and breakup) situation.

IV. DISCUSSION

A full theoretical description of the charge transfer processes which we have studied experimentally would require detailed knowledge of the relevant ion-atom potential-energy curves and the transition matrix elements for each of the reacting systems; these are not available. However, some insight into the experimental data may be gained by considering approximate potential curves obtained from the long-range ion-atom and ion-ion interactions and the known energy states of the separated particles.

Figure 1 depicts the general shape of the potential curves describing the $X^{2+} + Y$ initial state I of the system and the final $X^+ + Y^+$ states (one of these is indicated by F), as well as the energy levels of the separated-atom system. Owing to the induced-dipole ion-atom interaction, the initial state is slightly attractive, while the final states are strongly repulsive as a result of the Coulomb repulsion between the two positive ions. Crossing or pseudocrossings (depending on the symmetries of the two states) may occur at different internuclear separations, depending on the energy difference ΔE between the initial and final separated-atom states of the particles. For very large values of ΔE, crossings may be absent or may occur at energies not accessible to thermal energy particles, with the result that nonradiative charge transfer does not occur. However, radiative transitions from the initial state to lower final states (indicated by $h\nu$ on the diagram) may still provide a small probability for charge transfer.

For very small values of ΔE, crossings occur at such large internuclear separations that the overlap between the wave functions describing the initial and final states is very small and hence the probability of charge transfer is small. For single-electron transfer between atoms and doubly charged ions, the experimentally determined rate coefficients indicate that the optimal ΔE is of the order of 4 eV and that for $\Delta E < 2$ or >7 eV charge

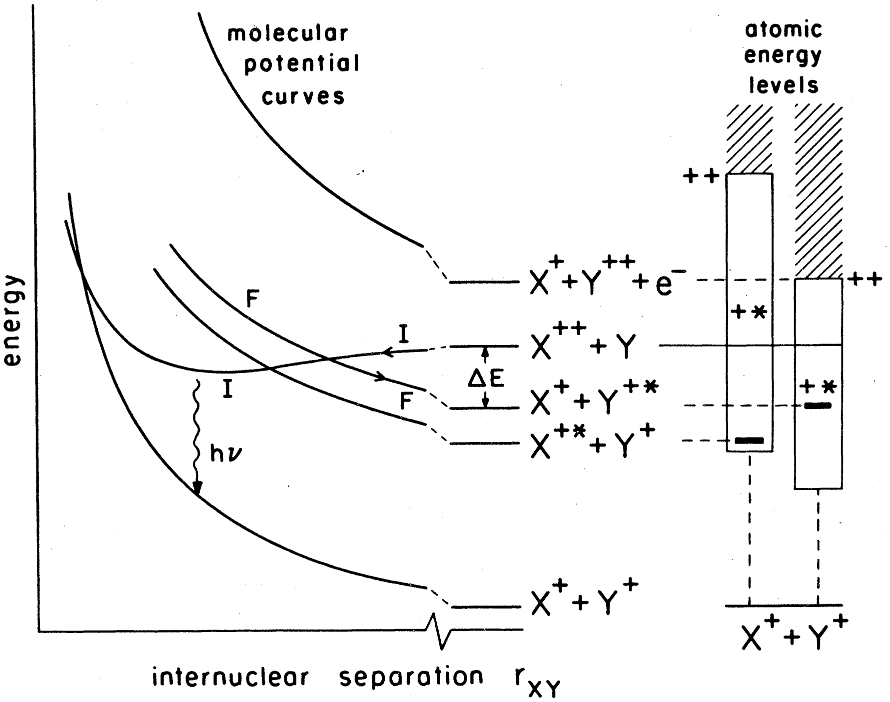

FIG. 1. Left-hand side: Schematic representation of hypothetical potential-energy curves involved in charge transfer reactions of the form $X^{2+} + Y \rightarrow X^+ + Y^+$. Right-hand side: Energy levels for the ions $X^+ + Y^+$ at large separation.

transfer usually occurs with very small probability (rate coefficients $\leq 10^{-4}$ the Langevin rate).

Figures 2–6 show actual separated-atom energy levels (corresponding to the hypothetical levels on the right-hand side of Fig. 1) which have a bearing on single-electron charge transfer between the various doubly charged rare-gas ions and the rare-gas atoms. The energy of the doubly charged parent ion (the sum of the first and second ionization potentials) is compared with the energy required to produce two singly charged ions or, in appropriate cases, a singly charged parent ion and a doubly charged reactant ion. The excited states of each ion are represented by a simplified-term diagram in the form of a box entending from the lowest excited state of the ion (^2S) to the ionization limit, while the continuum states representing a doubly charged product ion plus free electron are shown by cross-hatching.

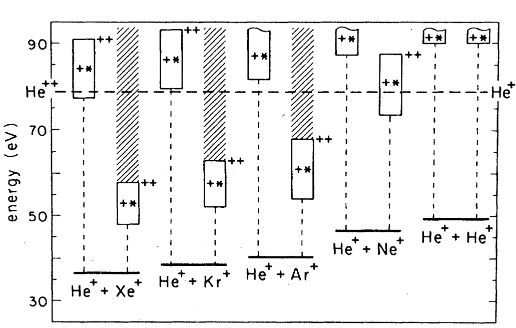

FIG. 2. Energy levels for charge transfer processes between He^{2+} ions and rare-gas atoms R, where R = Xe, Kr, Ar, Ne, and He. The boxes marked (+ *) schematically indicate the excited-state manifolds for singly charged ions, while the cross hatching indicates the continuum states of $R^{2+} + e^-$.

A. He^{2+} reactions

Figure 2 shows the energy levels pertaining to reactions of He^{2+} ions with various rare-gas atoms R. For R =Xe, Kr, and Ar, the energy of $He^{2+} + R$ lies well above that of $He^+ + R^{2+} + e^-$, so that *doubly* charged product ions can be formed by transfer ionization. As indicated in Table I, these reactions are found to be fast. In spite of the failure to observe Ar^{2+} product ions in argon (see discussion in Sec. III) transfer ionization rather than ordinary charge transfer is invoked, since the large energy defect for the latter reaction, $\Delta E > 11$ eV, makes the process unlikely. On the basis of the energy diagram, the reaction with neon would be expected to produce excited Ne^+ ions with high probability, consistent with our observation of a large rate coefficient. The reaction with helium would be expected to be slow, since no final states which meet the condition $2 < \Delta E < 7$ eV are accessible. Experimentally, the reaction is found to occur only as a very slow (radiative) process.[2]

B. Ne^{2+} reactions

As indicated in Fig. 3, Ne^{2+} ions can undergo transfer ionization to form doubly charged ions of

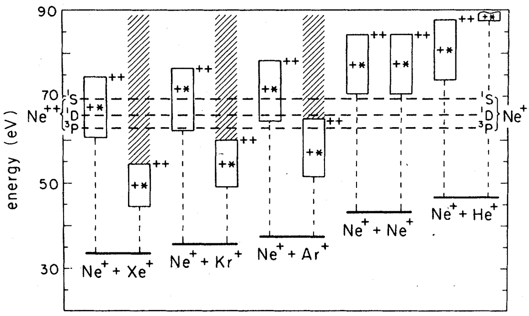

FIG. 3. Energy levels for the charge transfer processes $Ne^{2+}+R$. Same format as Fig. 2.

xenon, krypton, and argon (in the last case, only for Ne^{2+} ions in the ^1S or ^1D state); alternatively, formation of Ne^+ ions in excited states is possible. The experimental results (see Table II) indicate that in the case of the reaction with xenon, transfer ionization dominates over production of Ne^+ ions in excited states, with the exception of the reaction $Ne^{2+}(^3P)+Xe$, in which both channels appear to occur with comparable probability. The studies of the reactions with argon and with krypton gave somewhat inconclusive results because of the occurrence of secondary reactions of Ar^{2+} and Kr^{2+} with neon. However, Kr^{2+} ions were observed as products of the $Ne^{2+}+Kr$ reaction. The reactions of Ne^{2+} ions with neon and with helium are found to occur only through the slow, radiative charge transfer channel, as expected from the energy diagram.

C. Ar^{2+} reactions

The energy-level diagram of Fig. 4 indicates that production of doubly charged product ions by transfer ionization is not possible in thermal energy reactions of Ar^{2+} with any of the rare gases, and none is observed. Single charge transfer with xenon is found to be fast for all states of Ar^{2+}, apparently leading to production of Ar^+ or Xe^+ ions in excited states (see Table III). The reaction with krypton is found to be fast for $Ar^{2+}(^1S)$ ions only. Curve crossings for reactions of $Ar^{2+}(^1D)$ and $Ar^{2+}(^3P)$ with krypton should occur, but since ΔE for these states is either ≤ 2 or >13 eV, the crossings lie either at large internuclear distances (small overlap) or at small separations (endoergic for thermal energy particles), so that charge transfer does not occur.

Similarly, the reaction of $Ar^{2+}(^1D)$ with argon to produce $Ar^+(^2S)$ ions is exoergic by only about 0.1 eV, leading to a curve crossing at too large an internuclear separation to be effective in producing charge transfer; however, the apparent charge transfer coefficient seems to be considerably larger than expected for a purely radiative process. It is possible that the measured loss of $Ar^{2+}(^1D)$ includes quenching to the ^3P state (which is difficult to detect directly).

The reactions of $Ar^{2+}(^3P)$ with neon and helium are found to be quite fast, while those of $Ar^{2+}(^1S)$ are very slow, in keeping with the energy-defect criterion mentioned at the beginning of Sec. IV. In both cases ground-state Ne^+ and He^+ ions are the expected products of the reaction.

D. Kr^{2+} reactions

The energy levels pertaining to reactions of Kr^{2+} ions with rare-gas atoms are shown in Fig. 5. Charge transfer into excited states should occur in reactions with xenon and krypton (in the latter case, for ^1S ions only). If our suggested identification of the Kr^{2+} states is correct, the only case in which charge transfer is found to occur is $Kr^{2+}(^1S)+Xe$ (see Table IV), again in conformity with the ΔE criterion discussed previously.

Fast reactions of Kr^{2+} ions with neon are observed for all states of Kr^{2+}, indicating that favorable curve crossings to the state separating into ground-state product ions are present. The measured rate coefficient for $Kr^{2+}(^1S)$ with neon appears rather large considering the large exoergicity of this process (7.1 or 6.45 eV, depending on whether Kr^+ is produced in $^2P_{3/2}$ or $^2P_{1/2}$). It is possible

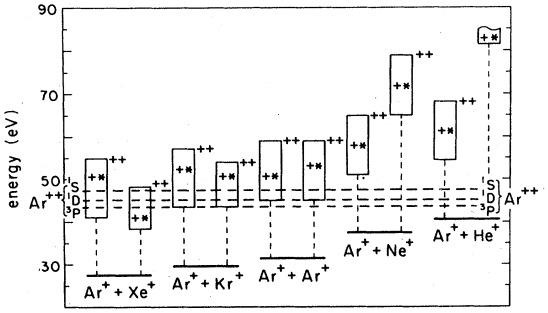

FIG. 4. Energy levels for the charge transfer processes $Ar^{2+}+R$. Same format as Fig. 2.

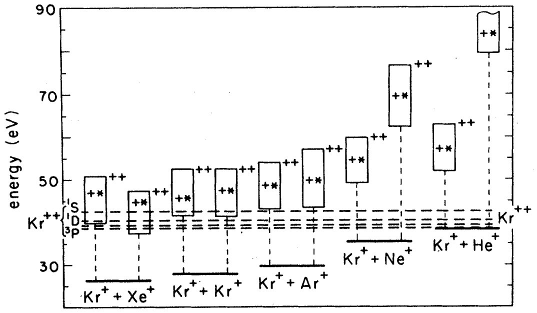

FIG. 5. Energy levels for the charge transfer processes $Kr^{2+}+R$. Same format as Fig. 2.

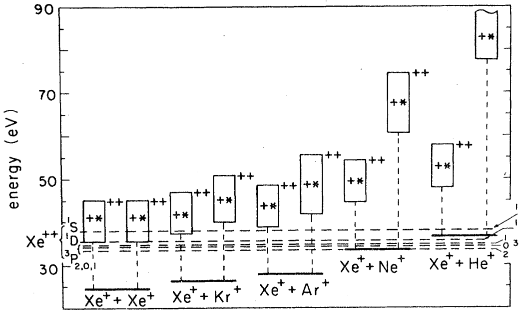

FIG. 6. Energy levels for the charge transfer processes $Xe^{2+}+R$. Same format as Fig. 2.

that quenching to the ^1D state (which would be difficult to detect experimentally) may precede charge transfer with neon. Also, some doubt remains concerning the identification of this state.

E. Xe^{2+} reactions

Figure 6 shows the energy levels for reactions of Xe^{2+} ions with rare gases. As indicated in Table V, the only moderately fast charge transfer reaction detected occurs with argon. The reaction was ascribed to the $^3P_2$ state of Xe^{2+}, since in this case only does the exoergicity appear small enough for a favorable curve crossing.

The identification of one of the Xe^{2+}-ion groups as containing ^1S ions raises questions as to why the reaction of $Xe^{2+}(^1S)$ with xenon is found to be slow ($<10^{-13}$ cm^3/sec), since reaction channels leading to excited Xe^+ ions should exist. However, the energy defect is small, $\Delta E \simeq 2$ eV, so that the curve crossings may occur at too large an internuclear separation for appreciable probability of nonradiative charge transfer.

F. Comparison with other measurements

To our knowledge, measurements at thermal energy of the reactions discussed here have not been carried out previously. Some preliminary results on Kr^{2+} and Xe^{2+} reactions with rare gases, obtained using a flowing afterglow apparatus,[6] have been made available to us. In some cases these agree quite well with the results presented here (the reactions of Xe^{2+} with argon, for instance). In other cases (the reaction of Kr^{2+} with neon), it appears that the afterglow measurements refer to an unresolved mixture of Kr^{2+} states, so that comparison with the present results is difficult.

Low-energy-beam experiments (0.5–100 eV) have been reported by Maier[7] on the reactions $Ne^{2+}+Kr$ and $Kr^{2+}+Ne$. The measurements indicate a steeply increasing cross section with decreasing energy at low energies, but the extrapolation to thermal energy is too uncertain for comparison with the present data. Both Kr^+ and Kr^{2+} ions were observed as products of the $Ne^{2+}+Kr$ reaction, which is compatible with the present results. The role of excited Ne^{2+} and Kr^{2+} ions which should have been present in the beam experiment is not clear. In another ion-beam experiment, Austin *et al.*[8] investigated collisions of He^{2+} ions with neon, argon, and krypton (at energies from 8 to 60 eV). They concluded that the $He^{2+}+Kr$ reaction produced Kr^{2+} ions only, that in collisions of He^{2+} with argon both Ar^+ and Ar^{2+} ions were produced, and that the reaction $He^{2+}+Ne$ resulted in Ne^+ ions only, in reasonable agreement with the present findings.

A detailed study by Niehaus and Ruf[9] of the electron energy spectrum resulting from transfer ionization in the reaction $He^{2+}+Hg$ at ion energies from 2 eV to 1 keV showed that molecular autoionization to form unstable $(HeHg)^{3+}+e^-$ which then dissociates into $He^++Hg^{2+}+e^-$, rather than atomic autoionization, is the process responsible for electron ejection in that reaction. A theoretical discussion of a similar process ($He^++Mg \rightarrow He+Mg^{2+}+e^-$) by Kulander and Dahler[3] also takes the view that molecular autoionization is the dominant mechanism in such reactions.

V. CONCLUSION

The present paper has described charge transfer processes between rare-gas atoms and doubly charged rare-gas ions in their ground (^3P) or low-lying metastable (^1D, ^1S) states. Empirically it is found that the reactions at thermal energy are fast if the exoergicity lies close to $\Delta E = 4$ eV, with a dramatic decrease in reaction rate generally observed when $\Delta E < 2$ or > 7 eV. This finding is compatible with our view of the charge transfer process as resulting from transitions at a crossing or avoided crossing of the initial- and final-state potential curves of the system. Studies at low energies of single-electron charge transfer and transfer ionization processes for the noble-gas ion-atom systems are not only of intrinsic interest but also provide valuable insight concerning the processes for astrophysically interesting ion-atom systems,[10] e.g., $Si^{2+}+H$, less susceptible to laboratory study. Further the charge transfer and quenching reactions described here provide a means for detecting or selectively destroying doubly charged noble-gas ions in specific excited states.

ACKNOWLEDGMENTS

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

[2] R. Johnsen and M. A. Biondi, Phys. Rev. A 18, 996 (1978).

[3] K. C. Kulander and J. S. Dahler, J. Phys. B 8, 460 (1975).

[4] K. Okuno, T. Koizumi, and Y. Kaneko, Phys. Rev. Lett. 40, 1708 (1978).

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

[6] F. C. Fehsenfeld (private communication).

[7] W. B. Maier, II, J. Chem. Phys. 60 , 3588 (1974).

[8] T. M. Austin, J. M. Mullen, and T. L. Bailey, Chem. Phys. 10, 117 (1975).

[9] A. Niehaus and M. W. Ruf, J. Phys. B 9, 1401 (1976).

[10] A. Dalgarno and S. E. Butler, Comments At. Mol. Phys. 7, 129 (1978).