Penning and associative ionization in the metastable neon-krypton system*

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Absolute and relative cross sections were obtained for the Penning-ionization (PI) reaction $Ne^* + Kr \rightarrow Ne + Kr^+ + e$ and the associative-ionization (AI) reaction $Ne^* + Kr \rightarrow NeKr^+ + e$. The studies were made by a merging-beams technique for a relative kinetic energy of the reactants from nominally 0.01 to 10 eV for PI and 0.01 to 0.6 eV for AI. The Ne* represents a composite of Ne($3s\ ^3P_2$) and Ne($3s\ ^3P_0$). At thermal energy the measured cross sections are compared with values obtained by beam-gas and beam-beam techniques.

INTRODUCTION

In a continuing effort to look at the role of the relative kinetic energy of reactants W in chemi-ionization reactions from near-thermal to higher energies, we have used merging beams to study the Penning-ionization (PI) reaction

$$Ne^* + Kr \rightarrow Ne + Kr^+ + e \quad (1a)$$

and the associative-ionization (AI) reaction

$$Ne^* + Kr \rightarrow NeKr^+ + e. \quad (1b)$$

The Ne* represents Ne($3s\ ^3P_2$) and Ne($3s\ ^3P_0$). These states have energies of 16.62 and 16.71 eV, respectively, and were not separated in the experiment. The PI reaction is exothermic by 2.62 eV for Ne($3s\ ^3P_2$) and by 2.71 eV for Ne($3s\ ^3P_0$).

Studies of reaction (1a) were made in the range $0.01 \leq W \leq 10$ eV by measuring the product Kr^+ current and lab-energy distributions of Kr^+. Cross sections for reaction (1b) were obtained over the range $0.01 \leq W \leq 0.6$ eV from measurements of the $NeKr^+$ current.

Laboratory energies of the species in these reactions will be designated by E with an appropriate subscript. For example, the lab energy of Ne* will be E_{Ne^*}.

EXPERIMENTAL

The merging-beams apparatus and the experimental technique and procedure for extracting data were similar to those described previously for a study of the Ne*-Ar system.[1] However, for that study both beams were modulated, whereas for the present experiment only one beam was modulated (at 100 Hz).

Electron bombardment sources 1 and 2 (see Ref. 1) were used for generating Ne^+ and Kr^+, respectively. The Kr^+ was converted to Kr in the first charge-transfer cell (see Ref. 1), which contained Kr. The Ne^+ was converted to neutral neon in the second charge-transfer cell, which contained Na vapor. The energy of Ne^+ was fixed at 1300 eV, and the energy of Kr^+ was adjusted to give the desired W.

BEAM COMPOSITION

The use of Kr in the first charge-transfer cell allowed a resonant charge-transfer reaction to occur in which ground-state Kr^+ from source 2 was converted to ground-state Kr. Since this reaction predominated in the cell, it is assumed that the Kr beam consisted of only ground-state particles.

The Ne beam consisted of Ne* and Ne ground-state [i.e., Ne($2p^6\ ^1S_0$)] particles. Excited species formed in the second cell in significant concentrations, other than the $^3P_{2,0}$ metastables, decayed to the ground state before reaching the interaction region. For our purposes, then, the composition of the Ne beam is given by the fraction f_g of Ne($2p^6\ ^1S_0$). The fraction of Ne($^3P_{2,0}$) is $(1 - f_g)$.

The f_g was determined by a technique recently developed in our laboratory for obtaining compositions of composite beams of rare-gas metastable and ground-state atoms. The method depends upon finding an ion-molecule reaction which proceeds for ground-state rare-gas atoms but not for metastables. The product-ion current I_c resulting from this reaction when the rare-gas reactant beam is a composite of ground-state and metastable species is divided by the product-ion current I_g (appropriately normalized) obtained when the rare-gas reactant beam is entirely in the ground state. The ratio I_c/I_g is the fraction f_g of ground-state species in the composite beam.

For the present work the reaction chosen was

$$HeD^+ + Ne \rightarrow NeD^+ + He. \quad (2)$$

For ground-state species this reaction is exothermic by approximately 0.25 eV, whereas for Ne* it is exothermic by almost 17 eV. We are not

aware of any studies in the literature of this reaction. Measurements of I_c and I_g were made in the merging-beams apparatus at $W = 1$ eV. The pure ground-state beam was obtained by charge transferring Ne^+ in Ne gas instead of Na vapor. For both measurements the detector was tuned to the same lab energy, i.e., that energy which produced an optimum NeD^+ current I_g.

For $E_{Ne} = 1300$ eV and a pressure of Na vapor in the cell of 0.5 mTorr (i.e., the pressure at which absolute cross-section measurements were made) we obtained $f_g = 0.49 \pm 10\%$. This f_g is 9% greater than the actual measured f_g to account for the secondary electron emission coefficient of Ne* being an assumed 16% greater than that for ground-state Ne.[1] We found that for Na pressures in the range 0.03–2 mTorr f_g is a decreasing function of pressure. Pressures quoted in this paper are accurate to within a factor of 2.

It seemed to us that reaction (2) was a good candidate for determining the composition of a composite Ne beam because its cross section for Ne* was likely to be negligible compared to that for ground-state Ne. The reasons for this are (a) the excess energy of the reaction with Ne* cannot be accommodated as internal energy in the products because of the unavailability of states, and (b) reactions are generally slow when internal energy of reactants has to be converted into kinetic energy of products.

To verify that reaction (2) was negligible with Ne* we compared measured lab-energy distributions of the product NeD^+ obtained from primary beams of composite and ground-state Ne. The shapes of the distributions for both types of beams were identical. If Ne* in the composite beam contributed a non-negligible signal, the distribution would have to be different from that for ground-state Ne since the internal energy of the Ne* can be converted only into kinetic energy of the products.

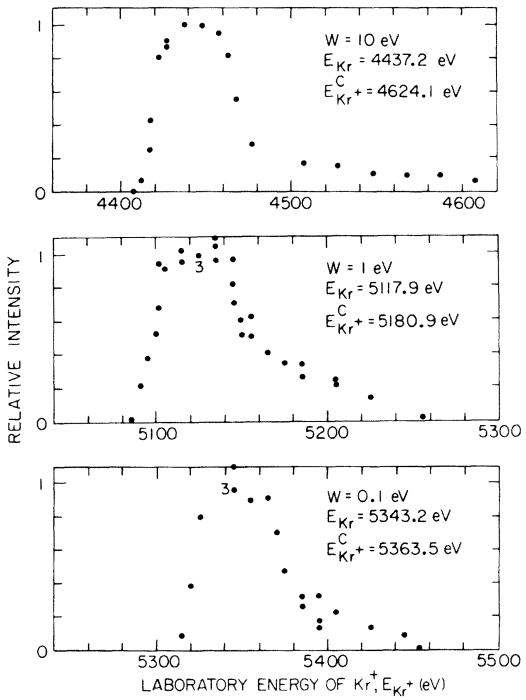

FIG. 1. Lab-energy distributions of Kr^+ production from Ne* + Kr. For all distributions Ne* is faster than Kr, and $E_{Ne^*} = 1300$ eV. The energy of Kr^+ if it had the velocity of the c.m. is designated as $E^c_{Kr^+}$. A digit adjacent to an experimental point represents the number of times that value was obtained.

RESULTS AND DISCUSSION

Energy distributions

The lab energy of $NeKr^+$ in reaction (1b) is monoenergetic, since this particle is formed by the coalescence of two heavy particles with the emission of an electron whose momentum is negligible. The lab velocity of $NeKr^+$ is equal to the velocity of the center of mass.

Laboratory-energy distributions of Kr^+ production from reaction (1a) are shown in Fig. 1. For a given W each distribution is very similar in shape to that for the previously reported study of PI of Ar by Ne*.[1] Information on the reaction kinetics for (1a) is inferred from the distributions in Fig. 1. The rationale for these deductions has been discussed for the Ne*-Ar experiment.[1] This information includes the following: (a) The reaction is directed with most of the Kr^+ scattered in the c.m. system approximately in the direction of the incident Kr; and (b) there is little momentum transfer in the c.m. system, so that the energy of the reactant Kr is about the same as that of the product Kr^+ and $W \approx W'$, where W' is the total relative kinetic energy of the heavy products.

Relative cross sections

Our relative cross sections Q for reaction (1) are shown in Fig. 2. Included are cross sections for AI and PI, which will be denoted as Q_{AI} and Q_{PI}, respectively. To relate the magnitudes of Q_{AI} and Q_{PI} to each other, the ratio $r = Q_{AI}/Q_{PI}$ was measured at $W = 0.1$ eV and will be designated $r(0.1)$. For this measurement E_{Ne^*} was again fixed at 1300 eV. The value of $r(0.1)$ was determined to be $0.24 \pm 10\%$. Also shown in Fig. 2 is our total ionization cross section Q_T, which is defined as $Q_T = Q_{AI} + Q_{PI}$. Above $W = 0.3$ eV, Q_T is essentially the same as Q_{PI}.

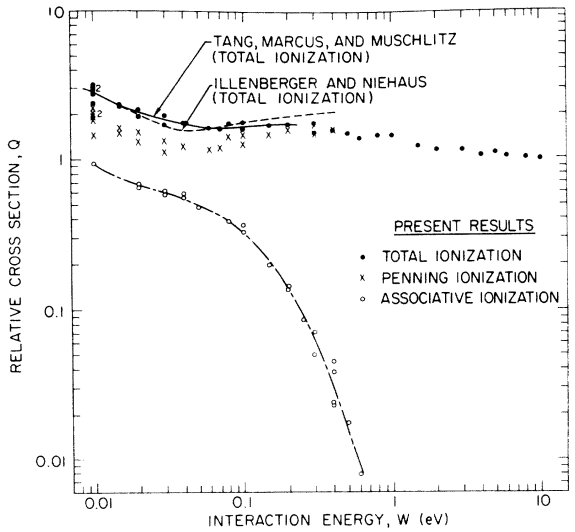

FIG. 2. Cross sections Q_{AI}, Q_{PI}, and Q_T relative to each other for Ne* + Kr collisions. The smooth curve through the AI points was drawn visually as the best fit to the data. $Q_T = Q_{AI} + Q_{PI}$, where the Q_{AI} are from this curve. A digit adjacent to a point represents the number of times that value was obtained. Included are the Q_T from a beam-gas experiment by Tang *et al.* (Ref. 3) and from a beam-beam experiment by Illenberger and Niehaus (Ref. 4).

We estimate that transverse velocities[2] increase our nominal, or quoted, W's in these experiments by an energy W_T no greater than 0.006 eV. A W_T = 0.006 eV could result in reductions of our Q of 21%, 8%, and 3% for nominal W's of 0.01, 0.03, and 0.1 eV, respectively. Random errors for Q_{PI} are larger for the smaller W's, where signal-to-noise ratios were smaller. It is estimated that these random errors are about ±15% for $W \leq 0.04$ eV and ±10% for $W > 0.04$ eV. Random errors for Q_{AI} are larger for the higher W's. It is estimated that these errors are ±10% for $W \leq 0.3$ eV and ±20% for $W > 0.3$ eV. Random errors in Q_T are about ±12% for $W \leq 0.04$ eV and ±10% for $W > 0.04$ eV.

Also shown in Fig. 2 are the Q_T obtained by Tang *et al.*[3] in a beam-gas experiment and the Q_T obtained by Illenberger and Niehaus in a beam-beam experiment.[4] The Q_T for all three experiments are in good agreement over the mutual range of W except near the highest energies of the Illenberger and Niehaus curve. Here the Illenberger and Niehaus Q_T appear to diverge from ours.

All of the Q_T show a minimum between $W = 0.01$ and 0.1 eV, which has been satisfactorily explained, for example, by Illenberger and Niehaus[4] and Hotop[5] on the basis of the so-called two-state potential curve model. The explanation is that the minimum is due to two opposing effects. One of these occurs at low W where the Ne*-Kr system is attractive (i.e., W is small compared to the well depth of the Ne*-Kr molecule). Here Q_T is controlled by the collision time, which, together with Q_T, decreases with increasing W. The other occurs at larger W where the system becomes repulsive, and the probability of ionization, and thus Q_T, increases with W. This increase is the result of an increase in the coupling width (an important parameter in the model) as the internuclear separation of the system decreases. The minimum in Q_T occurs in the region where the system changes from attractive to repulsive.

It should be noted that within the mutual errors of the experiments, the Q_{AI} in Fig. 2 is the same as our Q_{AI} for the Ne*-Ar system.[1]

TABLE I. Branching ratios and total ionization cross sections for collisions of $Ne(^3P_{0,2})$ with Kr.[a]

	Method	R[f]	Q_T (10^{-16} cm^2)
Present work	Merging beams	0.30 ± 0.05	$12.6^{+6.2}_{-5.3}$
Kramer *et al.*[b]	Beam-gas	0.32 ± 0.005	•••
Tang *et al.*[c]	Beam-gas	•••	4.1[h]
Niehaus[d]	Beam-beam	0.32 ± 0.02	•••
West *et al.*[e]	Beam-beam	0.30 ± 0.04[g]	17.6 ± 3.5[g]

[a] Except where noted quantities are for a relative collision energy of 0.05 eV.
[b] H. L. Kramer, J A. Herce, and E. E. Muschlitz, Jr., J. Chem. Phys. 56, 4166 (1972).
[c] Reference 3.
[d] A. Niehaus, Ber. Bunsenges. Phys. Chem. 77, 632 (1973).
[e] Reference 6.
[f] R is the associative ionization cross section divided by the total ionization cross section Q_T.
[g] For an effective collision temperature of 435 K.
[h] This value could be too low by as much as a factor of 3 because of an error in γ (Ref. 7).

Absolute cross sections and branching ratios

An absolute cross section Q_{abs} was measured for reaction (1b) at $W = 0.1$ eV and a pressure of Na vapor in the second cell of approximately 0.5 mTorr for which, as discussed previously, $f_g = 0.49$. The result is $Q_{AI}(0.1) = 2.5 \times 10^{-16}$ cm^2, with an estimated error of +47% and −40%. From this value and Fig. 2, Q_{abs} can be determined at all W for associative, Penning, and total ionization.

Shown in Table I are absolute Q_T's for the present experiment as well as for other experiments. Also shown is the branching ratio $R = Q_{AI}/Q_T$, which for our work can be obtained from Fig. 2. These quantities are for $W = 0.05$ eV or an average $\bar{W} = 0.05$ eV except for the work of West *et al.*[6] Their values represent an average over a range of relative energies associated with an effective collision temperature of 435 K. Since Q_T is not a rapidly changing function of W around 0.05 eV, it is reasonable to compare their Q_T with ours.

From Table I it is noted that the R's are in good agreement for all the experiments. The mean value of Q_T for West *et al.*[6] is about 40% higher than ours, but the error brackets overlap. The Q_T of Tang *et al.*[3] is low. We have been advised by Muschlitz[7] that his group has made some preliminary remeasurements of the secondary electron emission coefficient γ of the surface of Tang *et al.*[3] The result is that the new γ is about three times larger than the original value quoted in Ref. 3. This new γ would raise the Q_T of Tang *et al.*[3] by a factor of 3 and give good agreement with our mean value of Q_T.

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