Associative ionization in collisions between two excited reactants*

R. H. Neynaber and G. D. Magnuson
IRT Corporation, P. O. Box 80817, San Diego, California 92138
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Absolute and relative cross sections were obtained for the associative ionization (AI) reaction He* + Ne* → $HeNe^+$ + e by a merging-beams technique over a range of interaction energy W from 0.01 to 10 eV. The He* represents a composite of He($2\,^1S$) and He($2\,^3S$), and the Ne* a composite of Ne($3s\,^3P_2$) and Ne($3s\,^3P_0$). This study represents the first direct evidence of AI for which both reactants are excited. Studies were also made of the possible AI reaction Ne* + Ar* → $NeAr^+$ + e from thermal energy to 10 eV.

INTRODUCTION

A merging-beams technique has been used to study the associative ionization (AI) reaction

$$\text{He}^* + \text{Ne}^* \rightarrow \text{HeNe}^+ + e \qquad (1)$$

over a range of interaction energy W (i.e., relative kinetic energy in the center-of-mass system) from 0.01 to 10 eV. The He* represents He($2\,^1S$) and He($2\,^3S$), and the Ne* denotes Ne($3s\,^3P_2$) and Ne($3s\,^3P_0$). No state selection was made. Laboratory energies of the species in this reaction will be designated by E with an appropriate subscript. For example, the lab energy of He* will be E_{He^*}. For the experiment $E_{\text{He}^*} = 1100$ eV.

This study represents the first direct evidence of AI for which both reactants are excited.[1] However, $HeNe^+$ has been observed in an AI reaction where the reactants were identified as ground-state Ne and He in the $n=3$ state (the $n=2$ state did not react).[2,3] This mechanism for $HeNe^+$ formation did not exist in our experiment.

We also looked for AI for which the reactants were Ne* and Ar*, where Ar* represents metastable Ar($4s\,^3P_2$) and Ar($4s\,^3P_0$). This will be discussed after our study of reaction (1).

EXPERIMENT

A schematic of the apparatus is shown in Fig. 1. Helium ions were generated in source 1 and neon ions in source 2. The energy of the ionizing electrons was about 140 eV. The lab energy of Ne^+ (i.e., E_{Ne^+}) was adjusted to give the desired W (with Ne^+ usually slower than He^+). For the range of W covered in this experiment the range of E_{Ne^+} was 5458 to 4406 eV.

The Ne^+ beam was converted to a mixture of ground-state Ne and Ne* by passing it through the first charge transfer cell, which contained Na vapor. The He^+ beam was converted to a mixture of ground-state He and He* by passing it through the second charge-transfer cell, which contained Cs vapor. The neon neutral beam was partially attenuated in passing through the Cs in the second cell.

The reaction was studied by measuring the $HeNe^+$ current at the electron multiplier. The general method of extracting cross sections from such measurements of product ion currents has been described previously.[4] A potential could be applied to the interaction region so that only $HeNe^+$ formed inside the region could be detected.

BEAM COMPOSITION

In this section we attempt to determine the compositions of the helium and neon beams in the interaction region. These compositions are a factor in determining the absolute cross section Q_{abs} for reaction (1), and any error in the determination will be reflected in Q_{abs}. However, relative cross sections Q_R depend only on the compositions remaining fixed over the range of W covered in the experiment. We thus expend some effort in assessing the constancy of the compositions.

In a previous study of the rearrangement-ionization (RI) process[5] He* + H_2 → HeH^+ + H + e arguments were presented for invoking a statistical distribution for the formation of helium neutrals in the Cs cell in singlet and triplet states. Although E_{He^*} for this experiment is less than the 4000 eV used in that study and higher energies favor a statistical distribution,[6,7] it appears from the work of Olson and Smith[6] that the distribution is close to statistical for $E_{\text{He}^*} \gtrsim 1000$ eV. Assuming a statistical distribution, we conclude, by an analysis similar to that used in the RI experiment, that in the interaction region the helium beam essentially consisted of He($2\,^1S$), He($2\,^3S$), and He($1\,^1S$) in the ratios 1 : 10.5 : 3. These ratios are only slightly different from those for the RI study because different charge-transfer cross sections were assumed due to the lower E_{He^*}. This analysis also shows that the population of $n=3$ states of helium should be negligible compared to that of $n=2$ states because

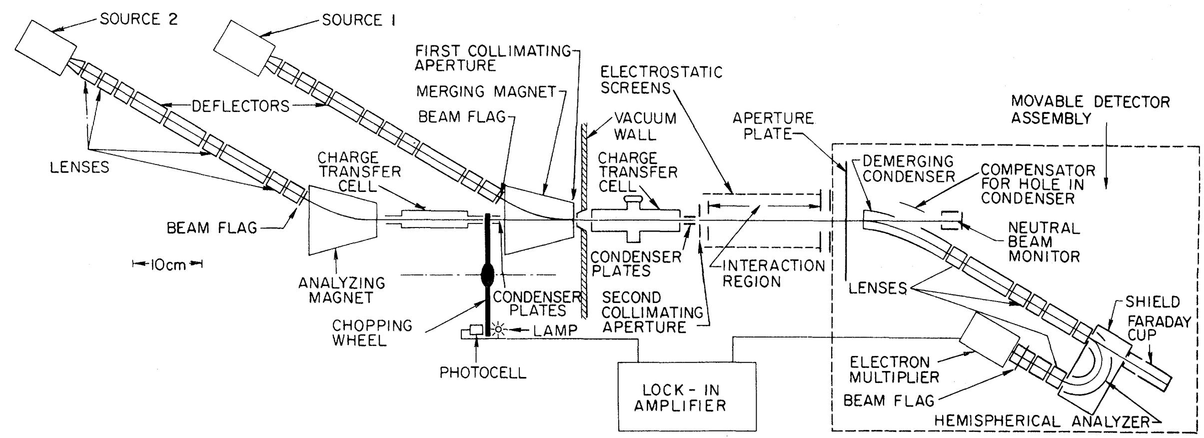

FIG. 1. Schematic of merging-beams apparatus. Apertures are not to the scale shown.

(i) energy defects are considerably larger for charge transfer of He^+ to He($n=3$) than to He($n=2$) and (ii) transit times from the charge-transfer cell to the interaction region are from 3 to 100 times longer than lifetimes of $n=3$ states for transitions to $n=2$ or $n=1$ states.

We also assume a statistical distribution for the formation of neon neutrals in the Na cell as was done for our previous studies of collisions of Ne* with Ar.[8] In those studies $E_{Ne*}=2750$ eV, which is considerably less than E_{Ne*} for the present experiment. Our assumption of such a distribution for this study would appear to be better than for the Ne*-Ar effort since E_{Ne*} is larger here. We can conclude from this assumption, using an analysis described for the Ne*-Ar investigations,[8] that the composition of the neon beam prior to its passage through the second charge-transfer cell consisted of Ne($3s\,^3P_2$), Ne($3s\,^3P_0$), and Ne($2p^6\,^1S_0$) in the ratios 5 : 1 : 6. If, in the second cell, the percentage attenuation of these species were different (hereafter referred to as selective attenuation of neon), then the composition in the interaction region would be different. This possibility will be considered later in discussions of Q_{abs} and Q_R for reaction (1).

If our analysis of the composition of the helium beam were incorrect and there were a significant concentration of He($n=3$), then $HeNe^+$ might be formed by AI with ground-state Ne, as observed by others and mentioned above.[2,3] To test for this possibility, we replaced the Na vapor in the neon charge-transfer cell with Ne so that a beam of virtually all ground-state Ne was generated. No $HeNe^+$ was observed when this beam was merged with our excited helium beam. We conclude that the observed $HeNe^+$ in our studies resulted from collisions of excited helium and excited neon.

There is no question that the composition of the helium beam remained fixed for the Q_R data because all parameters associated with its generation over the entire W range of the Q_R curve were kept constant. On the other hand, over this range E_{Ne+} was varied between 5458 (for $W=0.01$ eV) and 4406 eV (for $W=10$ eV), a change of about 19%. Errors would be introduced in Q_R if the probability for generation of Ne* in the first charge-transfer cell changed over this range of E_{Ne+} and/or if selective attenuation of neon in the second cell changed over this range. If these factors are not steep functions of E_{Ne+}, these errors will not be large since the variation of E_{Ne+} is moderate. For example, the E_{Ne+} for $W=1$ and 5 eV are, respectively, only 6 and 14% less than that for $W=0.01$ eV.

To learn more about the composition of the beams, we observed the dependence of the effective cross section Q_{eff} for reaction (1) (i.e., cross section for the composite beams including ground-state species) at $W=0.01$ eV on the vapor pressure p_1 of Na in the first charge-transfer cell and on the vapor pressure p_2 of Cs in the second. There was no dependence of Q_{eff} over the range of p_1 studied, viz., 2.3×10^{-4} Torr $\le p_1 \le 1.5\times10^{-3}$ Torr. This suggests that the composition of the neon beam did not change in this range. For optimum signal-to-noise when Q_{abs} and Q_R were being measured, p_1 was normally adjusted to about 1.5×10^{-3} Torr.

We observed that Q_{eff} monotonically decreases with increasing p_2 over the range $3\times10^{-5} \le p_2 \le 1.2\times10^{-3}$ Torr, although it appears to be flattening out at the lower p_2. (For optimum signal-to-noise p_2 was normally adjusted to about 4.3×10^{-4} Torr.) This indicates that the composition of the neon and/or helium beam changed with p_2 in this range and that selective attenuation of neon and/or helium occurred. To determine the possible effects of such attenuation on Q_R, we made Q_R measurements over the range $0.01 \leq W \leq 0.7$ eV at various p_2. We observed no dependence of Q_R on p_2. Problems associated with signal-to-noise prevented us from extending these tests to higher W.

In a different experiment we observed that the composition of an excited helium beam (formed by charge transfer of He^+ in Cs) at 1400 eV did not change when the vapor pressure of Cs was varied between 4.9×10^{-4} and 1.5×10^{-3} Torr. This indicates that there is no significant selective attenuation of helium as a function of Cs pressure at 1400 eV. From this observation, we think it is unlikely that selective attenuation of helium is important at 1100 eV. This suggests that the selective attenuation by Cs observed in the present experiment is that of neon and could be due to stripping of Ne* by Cs and/or Penning ionization of Cs by Ne*.

The effect on Q_R of changes in the selective attenuation of neon with W have been discussed above. The effect on Q_{abs} of such attenuation has been eliminated by extrapolating the Q_{eff}-vs-p_2 curve to zero pressure. This will be discussed in more detail later.

RESULTS AND DISCUSSION

The lab energy of $HeNe^+$ in reaction (1) 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 $HeNe^+$ is equal to the velocity of the center of mass.

Relative cross sections Q_R for the reaction are shown in Fig. 2. Random errors are larger for the higher W. It is estimated that these errors are ±20% for $W \leq 0.5$ eV, ±25% for $0.5 < W \leq 5$ eV, and ±100% for $W = 10$ eV. We estimate that transverse velocities[9] increase our nominal, or quoted, W's by an energy W_T no greater than 0.005 eV. A $W_T = 0.005$ eV could result in percentage reductions of Q_R of 18, 7, and 2 for nominal W's of 0.01, 0.03, and 0.1, respectively.

Included in the figure are a few points obtained by replacing Cs in the second cell with Na. The pressure of the Na vapor was 5.3×10^{-4} Torr. These points agree with the others within experimental error. An analysis of the composition of the helium beam in the interaction region similar to that used for Cs in the cell indicates ratios of $He(2\,^1S) : He(2\,^3S) : He(1\,^1S) \approx 1 : 14 : <1$. Extensive studies with Na were not conducted because the intensity of the helium beam was considerably smaller than was obtained with Cs.

The striking feature of the Q_R data in Fig. 2 is the peak at about $W = 1.5$ eV. Perhaps near 1.5-eV transitions to a different potential curve or curves of the molecular system occur and this results in an increase in Q_R. There are many energy levels near the metastable states of helium and neon which must give rise to a variety of such potential curves.

Included in the figure are our Q_R for the reactions

$$He^* + H(D) \rightarrow HeH^+(HeD^+) + e \,, \qquad (2)$$

which we previously studied.[10] These Q_R have been normalized to the average Q_R for reaction (1) at $W = 0.05$ eV. No Q_R for reactions (2) were measured below this W. We include these data because we think it interesting that the Q_R for (1) and (2) are essentially the same from $W = 0.05$ eV up to the beginning of the peak associated with (1). It is not clear what mechanism, if any, is common to these reactions which would account for this fact. However, the absence of peaks for (2) could be explained by an understandably smaller number of potential curves to which transitions of the molecular systems could occur.

A Q_{abs} of reaction (1) was determined at $W = 0.1$ eV, $p_1 = 1.5 \times 10^{-3}$ Torr, and $p_2 = 4.3 \times 10^{-4}$ Torr. At this p_2 there was selective attenuation, which reduced Q_{eff} by about 40%. This percentage was determined, as mentioned previously, by extrapolating the Q_{eff}-vs-p_2 curve to zero pressure.

The value of Q_{abs}, corrected for attenuation, is $Q_{abs}(0.1) = 1.2 \times 10^{-17}$ cm^2 with an estimated error of +60% and −53%. This is for composites of $Ne(3s\,^3P_2)$ and $Ne(3s\,^3P_0)$ in the ratio 5 : 1 and

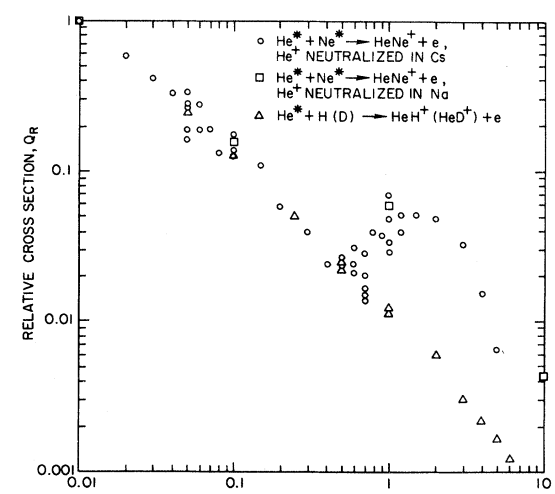

FIG. 2. Relative cross sections Q_R for $He^* + Ne^* \rightarrow HeNe^+ + e$. Included for comparison are Q_R for $He^* + H(D) \rightarrow HeH^+(HeD^+) + e$. The Q_R for the $He^* + Ne^*$ reaction are normalized to unity at $W = 0.01$ eV. The Q_R for the $He^* + H(D)$ reaction are normalized to the average Q_R for the $He^* + Ne^*$ reaction at $W = 0.05$ eV.

He($2\,^1S$) and He($2\,^3S$) in the ratio 1 : 10.5. If the cross section of reaction (1) for He($2\,^1S$) is considerably less than 10.5 times that for He($2\,^3S$), then the value of Q_{abs} quoted above is approximately the same for the composite Ne* reactant and He($2\,^3S$). At $W = 0.1$ eV the Q_{abs} for each reaction of (2) is more than an order of magnitude larger than Q_{abs} for reaction (1).

ADDITIONAL STUDIES

As mentioned previously, we also studied the possible reaction

$$\mathrm{Ne}^* + \mathrm{Ar}^* \rightarrow \mathrm{NeAr}^+ + e\ . \tag{3}$$

Neon ions were generated in source 1 and argon ions in source 2. Sodium was used in the second charge-transfer cell to convert Ne^+ to excited neon, and Cs was used in the first cell to convert Ar^+ to excited argon. For this experiment $E_{\mathrm{Ne}^*} = 2750$ eV and E_{Ar^*} was adjusted for the desired W.

There was no evidence for selective attenuation of either beam. In the interaction region the neon beam consisted of Ne($3s\,^3P_2$), Ne($3s\,^3P_0$) and Ne($2p^6\,^1S_0$) in the ratios 5 : 1 : 6. These ratios were calculated by the method described previously. Using this same method, we determined that the argon beam consisted of Ar($4s\,^3P_2$), Ar($4s\,^3P_0$), and Ar($3p^6\,^1S_0$) in the ratios 5 : 1 : 6.[11]

In order to estimate the cross section for reaction (3) we compared its Q_{eff} with that from the process

$$\mathrm{Ne}^* + \mathrm{Ar}(3p^6\,^1S_0) \rightarrow \mathrm{NeAr}^+ + e\ , \tag{4}$$

which we previously studied.[8] At $W = 0.05$ eV the ratio of Q_{eff} for reaction (3) to that of (4) is $Q_{eff}^{(3)}/Q_{eff}^{(4)} \approx \frac{2}{3}$. This results in a ratio of the actual cross section of (3) to (4) of $Q_3/Q_4 \approx \frac{1}{3}$. This ratio is fairly sensitive to the assumed compositions of the neon and argon beams and to the ratio $Q_{eff}^{(3)}/Q_{eff}^{(4)}$. We estimate the following bounds: $0 \le Q_3/Q_4 \le 0.4$.

To further study reaction (3) we determined the dependence of $Q_{eff}^{(3)}$ on W by making measurements at $W = 0.05$, 0.2, 0.5, 1, 5, and 10 eV. We compared this dependence with that for reaction (4), which we obtained from previous studies[8] and some additional measurements. The dependences are the same. This indicates that either (a) the shapes of the actual cross-section curves for the two reactions are the same or (b) Q_3 is zero or so small compared to Q_4 that its effect cannot be observed. It seems unlikely that the shapes would be identical over the entire range of W from 0.05 to 10 eV. Therefore, the latter interpretation seems more reasonable to us. The fact that a $Q_{eff}^{(3)}$ can be measured at all could simply be due to the ground-state component of the Ar beam [i.e., Ar($3p^6\,^1S_0$)] giving rise to a signal associated with reaction (4).

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