Luminescence from low-energy He^+/Xe charge-transfer reactions

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Optical emissions produced by collision of 100-eV He^+ ions with Xe atoms have been studied over the spectral range from 40 to 900 nm. All of the major lines in the emission spectrum can be assigned to transitions in Xe II resulting from charge-transfer reactions. Emission cross sections for the major lines in the vacuum-ultraviolet and visible spectral regions are reported and the importance of cascading is assessed. The kinetic energy dependence is discussed for several of these lines.

INTRODUCTION

Charge transfer has recently been shown to be an efficient pumping mechanism for certain laser systems.[1,2] In this laboratory, luminescence from ion-neutral reactions having potential laser applications has been investigated. Part of this study has focused on reactions of He^+ with rare gases.[3-5] These reactions are of particular interest because of the earlier reports by Lipeles *et al.*[6] of vacuum-ultraviolet (VUV) and visible emissions from these reactions at relatively low interaction energies. However, no spectral assignments or cross-section measurements for the production of specific states were made by these authors for the He^+/Xe system. In this communication, we will report assignments and cross sections for some of the major lines in the visible and vacuum ultraviolet regions.

EXPERIMENTAL

A. Apparatus

The emission spectra and the translational energy dependences of selected spectral lines were obtained using a previously described[3] beam-spectrometer apparatus constructed in our laboratory. Briefly, the apparatus consists of a single focusing mass spectrometer with conventional electron impact source which is utilized to produce a mass-resolved ion beam and transmit it into a collision chamber. The apparatus incorporates differential pumping in order to minimize collisions of the projectile ion beam in the region between the ion source and the collision chamber. The energy and focal point of the ion beam are controlled by a decelerating lens positioned immediately ahead of the collision chamber. This is a four-element slot lens which slows the ions from 170 eV, as they exit the mass spectrometer, to the desired interaction energy, as low as 1.0 eV (lab) with uncertainty represented by an energy spread of 1 eV (FWHM). Some of the photons produced in the collision chamber pass through the ion exit slit and enter a McPherson 1-m VUV monochromator. The monochromator is equipped with a variety of gratings and photomultiplier detectors to permit monitoring a broad spectral region. The output from the photomultiplier detectors is pulse counted using an SSR Model 1110 photon counter.

With the experimental configuration described, the monochromator views along the axis of the ion beam, and some of the radiation collected originates from collisions occurring in the region of the decelerating lens, where the He^+ ion energy is higher than at the collision chamber. To determine an appropriate background correction factor, the ion beam is deflected immediately in front of the collision region, thereby eliminating reaction in the collision chamber, however, not affecting reactions occurring within the deceleration lens. The resulting photon count is then subtracted from the total photon count observed while the ion beam is traversing the collision chamber. This correction varies from 10 to 30% depending on the energy dependence of the emission.

B. Operating conditions

The He^+ ion flux was 2.5×10^{11} ions cm^{-2} sec^{-1} (current of 40 nA cm^{-2}) and Xe atom density was 1.6×10^{14} atoms cm^{-3} (5-mTorr pressure at room temperature) in the interaction region. The pressure was measured using an MKS Baratron capacitance manometer directly coupled to the collision region. For isotropic photon emission, typically 1 out of 2000 photons strikes the monochromator grating.

C. Calibration

In the VUV region, cross sections were calculated using the best available data for detector quantum efficiency. Both Bendix Channeltron[7] and EMR 541-F[8] detectors were used. Namioka and Hunter[9] have reported an absolute reflectance of 4% at 121.6 nm for a gold-coated grating. Samp-

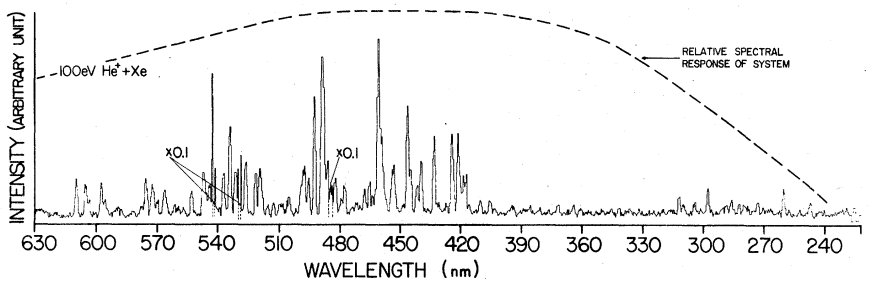

FIG. 1. Optical emissions observed in the visible spectral region from the reaction of 100-eV He^+ ions with Xe. Optical resolution is 2 nm. *Note*: When output from the digital counter exceeds full scale on the recorder, it is automatically reduced by a factor of 10 for plotting.

son[10] has shown platinum to have a reflectance of about 1.4–1.5 times that of gold. On this basis and consistent with reports of Zaidel and Shreider[11] we have estimated a reflectance of 6% at 121.6 nm. Using these assumptions we find that the calculated cross section of 0.60 Å^2 for Lyman-α production (121.6 nm) from impact of a 100-eV He^+ ion beam on hydrogen compares favorably with the accepted value of 0.44 Å^2 derived by Dunn, Geballe, and Pretzer.[12] The relative spectral reflectances were interpolated from the data of Namioka and Hunter at 121.6, 58.4, and 30.4 nm.

An absolute calibration of the monochromator was made in the 450–900 nm region for each grating, using an NBS-calibrated tungsten strip lamp, based on the method outlined by Kostkowski and Lee.[13] Below 450 nm, the internally reflected light was equal to or greater than the light emitted by the tungsten lamp. Therefore, the relative grating reflectance[14] and photomultiplier quantum efficiency[15] between 250 and 450 nm were used to determine a relative instrument function. This function was normalized at 450 nm to the absolute value obtained from the NBS-calibrated lamp.

Errors are estimated to amount to ±30% uncertainty in the relative values of the emission cross section and a factor of 2 to 3 in the absolute values.

RESULTS AND DISCUSSION

Emission spectra observed in the visible and VUV regions from impact of 100-eV He^+ ions on Xe are shown in Figs. 1 and 2. These were obtained with the monochromator slits adjusted for a spectral resolution of about 2 nm. Higher-resolution spectra (0.2 nm) have also been obtained for most of the intense lines. The raw data were reduced using a computer program which compares the observed spectral lines with transitions expected on the basis of known energy levels in the HeI, XeI, and XeII systems.[16] About 95% of the emissions observed in the VUV can be unequivocally assigned to specific transitions, but many of the lines observed with high resolution in the visible can be assigned to more than one transition. In assigning the states listed in Tables I and II, all wavelengths calculated by the computer search routine for Xe II transitions which do not violate the selection rule $\Delta J = 0, \pm 1$ or Laporte's rule, are included. None of the observed lines could be positively identified with HeI or XeI transitions.

The dependences of the cross sections for several of the major emissions upon He^+ translational energy were also determined. The major line observed in the visible region (484.6 ± 0.2 nm), was found to exhibit an energy threshold which is below 10 eV (c.m.). Only one transition can be identified which is consistent with this threshold, that is, $6s\ ^4P_{5/2} - 6p\ ^4D^o_{7/2}$. Other J combinations within this band can be recognized among the possible assignments that are summarized in Table I. Table I includes all possible transitions for the five wavelengths listed, consistent with the spectral resolution. From relative emission cross sections[17] and relative transition probabilities,[18] we infer that the transition $6s\ ^4P - 6p\ ^4D^o$ is the major contributor to the emission cross section at these wavelengths. The same five transitions (J combinations) have also been observed in this laboratory in the analogous He^+/Kr system. It is interesting to note that of the five assigned transitions listed in Table I, two are among the strong-

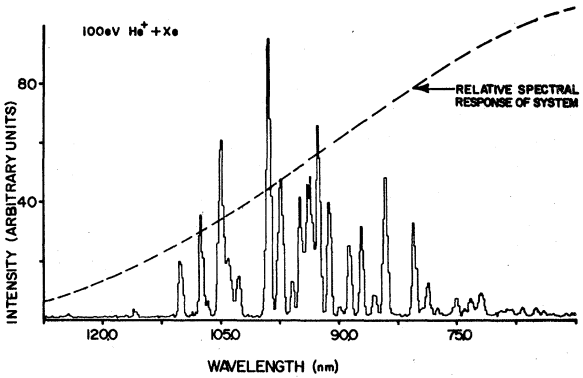

FIG. 2. Optical emissions observed in the VUV from the reaction of 100-eV He^+ ions with Xe. Optical resolution is 2 nm.

TABLE I. Xe II transitions observed in the visible spectral region from the reaction of 100-eV He^+ with Xe.

Observed wavelength [a] λ_0 (nm)	Total cross section for observed emission [b] (10^{-18} cm)	Possible assignments, Xe II Lower	Upper	$\lambda_T-\lambda_0$ [c] (nm)	ΔH [e] (eV)
$484.6_3 \pm 0.2$	6.4	$6s\,^4P_{5/2}$	$6p\,^4D^o_{7/2}$	−0.06	1.64
$542.1_8 \pm 0.2$ [d]	5.6	$6s\,^4P_{3/2}$	$6p\,^4D^o_{5/2}$	−0.11	1.62
$421.5_8 \pm 0.2$	1.9	$6s\,^4P_{5/2}$	$6p\,^4D^o_{3/2}$	0.10	2.02
		$5d\,^2P_{1/2}$	$6p'\,^2P^o_{3/2}$	0.01	3.62
		$6p\,^4D^o_{1/2}$	$6d\,^4P_{3/2}$	−0.10	5.41
$460.4_8 \pm 0.2$ [d]	4.2	$6s\,^4P_{3/2}$	$6p\,^4D^o_{3/2}$	−0.05	2.02
		$5d\,^4F_{5/2}$	$6p\,^2P^o_{3/2}$	−0.05	2.83
$519.3_3 \pm 0.4$	1.1	$6s\,^4P_{1/2}$	$6p\,^4D^o_{1/2}$	−0.05	2.47
		$5d\,^2P_{3/2}$	$6p\,^2P^o_{1/2}$	−0.06	2.99
		$6p\,^4P^o_{1/2}$	$2_{1/2}$	0.31	4.02
		$6p\,^4S^o_{3/2}$	$6d\,^4P_{1/2}$	0.03	5.01
		$6p\,^2D^o_{5/2}$	$7s\,^2P_{3/2}$	−0.38	5.20

[a] Calculated in vacuum.
[b] The calculation of these values assumes isotropic photon emission and neglects possible polarization effects.
[c] λ_T, calculated from levels listed in Ref. 16, is the wavelength corresponding to the assigned transition.
[d] These are among the strongest lines observed in the xenon ion laser (see Ref. 19).
[e] Enthalpy change for the reaction $He^+ + Xe \rightarrow He + Xe^{+*}$.

TABLE II. Major emissions observed in the VUV from reaction of 100-eV He^+ with Xe.

Observed wavelength [a] λ_0 (nm)	Total cross section for observed emission [b] (10^{-18} cm^2)	Possible assignments, Xe II Lower	Upper	$\lambda_T-\lambda_0$ [c] (nm)
93.13 ± 0.1	5.2	$5p^5\,^2P^o_{3/2}$	$5d\,^4P_{3/2}$	0.00
93.52 ± 0.1	7.8	$5p^5\,^2P^o_{3/2}$	$5d\,^4P_{1/2}$	0.02
93.95 ± 0.1	9.5	$5p^5\,^2P^o_{3/2}$	$5d\,^4P_{5/2}$	−0.03
94.42 ± 0.1	5.4	$5p^5\,^2P^o_{3/2}$	$5d\,^2P_{1/2}$	−0.03
94.98 ± 0.1	9.4	$5p^5\,^2P^o_{3/2}$	$5d\,^2P_{3/2}$	−0.03
98.90 ± 0.1	28.5	$5p^5\,^2P^o_{3/2}$	$6s\,^4P_{1/2}$	−0.04
103.25 ± 0.2	1.7	$5p^5\,^2P^o_{3/2}$	$5d\,^4D_{1/2}$	−0.01
		$5p^5\,^2P^o_{1/2}$	$5d\,^4P_{3/2}$	0.01
103.81 ± 0.1	4.7	$5p^5\,^2P^o_{1/2}$	$5d\,^4P_{1/2}$	−0.04
104.83 ± 0.1	25.3	$5p^5\,^2P^o_{3/2}$	$5d\,^4D_{5/2}$	0.00
		$5p^5\,^2P^o_{1/2}$	$5d\,^2P_{1/2}$	−0.01
105.22 ± 0.1	10.4	$5p^5\,^2P^o_{3/2}$	$6s\,^4P_{3/2}$	−0.03
107.47 ± 0.1	16.5	$5p^5\,^2P^o_{3/2}$	$6s\,^4P_{5/2}$	−0.02

[a] Calculated in vacuum.
[b] The calculation of these values assumes isotropic photon emission and neglects possible polarization effects.
[c] λ_T, calculated from levels listed in Ref. 16, is the wavelength corresponding to the assigned transition.

est lines observed in the cw xenon-ion laser.[19]

The VUV emissions shown in Fig. 2 can all be assigned to XeII transitions. Table II is a summary of some of the more intense lines. This includes all of the observed transitions from $6s\,^4P$, $5d\,^4P$, and $5d\,^2P$ states. The cross section of the most intense line in the VUV (98.90 nm) was found to be constant over the energy range 20–140 eV. In constrast, emissions monitored over the interval 97.3 ± 1 nm as shown in Fig. 3 exhibit a strong kinetic energy dependence. There are two lines, 97.34 nm ($5p^5\,^2P^o_{3/2} - 6s\,^2P_{3/2}$) and 97.70 nm ($5p^5\,^2P^o_{1/2} - 6s'\,^2D_{3/2}$) contributing to this curve. The maximum, occurring at 12 eV (lab), corresponds to a cross section of ~0.4 Å^2. Lipeles *et al.*[6] observed a similar dependence in the total cross section for photon production in the range 20–120 nm. The total cross section obtained by summing the emission cross sections (100-eV He^+ ion impact) of all individual lines in this interval is 2.4 Å^2 which is about one-half the apparent cross section observed by Lipeles *et al.*[6] De Heer and co-workers[20,21] have studied this reaction at higher energies and have obtained a total cross section[21] of 3.6 Å^2 over this interval for impact of 300-eV He^+ ions.

A detailed study of the excitation mechanism for the $6s\,^4P$, $5d\,^4P$, and $5d\,^2P$ states is summarized in Table III. The energetics of formation of each of the possible J levels of the ^4P and ^2P states of XeII from ground-state He^+ and Xe reactants are listed. In addition, the total emission cross section for radiation to the $5p^5\,^2P^o_{3/2}$ and $5p^5\,^2P^o_{1/2}$ ground ionic states (determined from VUV emission cross sections) is shown, along with the total cascading cross section from high-energy states to those individual states (determined from visible emission cross sections). The last column is the difference between the measured emission cross section in the VUV and the measured cascading cross sections in the visible region for each individual state populated and thus is the cross section for direct formation of the states indicated in Table III formed in the original ion-neutral collision. As can be seen, the first two states listed in Table III are formed mainly by populating higher-energy states, followed by cascading, rather than directly in the ion-neutral collision. This is in agreement with the findings of De Heer

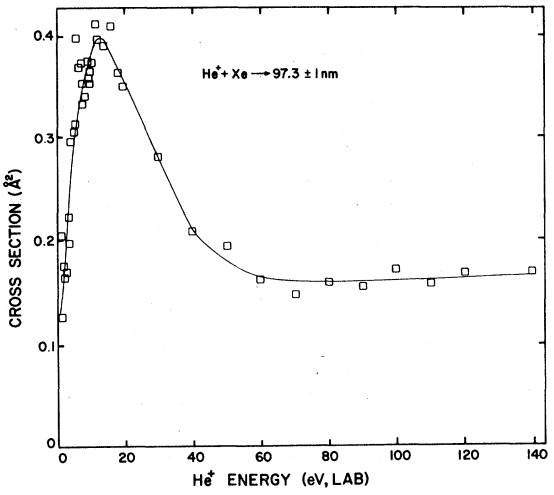

FIG. 3. Emission cross section for XeII radiation observed within the interval 97.3 ± 1 nm from impact of He^+ ions on Xe.

TABLE III. Total emission and cascading cross sections for the major XeII ^4P and ^2P states observed in the He^+/Xe reaction.

State, XeII	ΔH [a] (eV)	Cross sections (10^{-18} cm^2) Total emission	Cascading	Direct formation
$6s\,^4P_{5/2}$	−0.92	16.5	15.1	1.4
$6s\,^4P_{3/2}$	−0.67	10.4	12.0	−1.6
$6s\,^4P_{1/2}$	0.09	28.5	1.2	27.4
$5d\,^2P_{3/2}$	0.60	9.4	0.4	9.05
$5d\,^2P_{1/2}$	0.68	18.1 (12.7) [b]	•••	18.1
$5d\,^4P_{5/2}$	0.74	9.5	4.6	4.9
$5d\,^4P_{1/2}$	0.80	12.5	0.6	12.0
$5d\,^4P_{3/2}$	0.86	6.1 (0.9)	•••	6.1

[a] Enthalpy change for the reaction $He^+ + Xe \rightarrow He + Xe^{+*}$.

[b] There is an uncertainty on the order of ±12.7 in this value because of unknown contribution of the unresolved transition $5p^5\,^2P^o_{3/2} \leftarrow 5d\,^4D_{5/2}$. Tabulated value assumes approximately equal contribution from each transition.

and co-workers[21] at 300-eV He^+ ion energy. However, in contrast, the $6s\ ^4P_{1/2}$ state is almost entirely formed directly in the ion-neutral collision. Radiation from this state constitutes more than 7% of the total radiation produced in the reaction. Similarly, the remaining states listed in Table III, which are also populated by processes which are endoergic for ground-state reactants, are formed directly in the ion-neutral collision. The total cross section for those emissions listed in the table approaches one-third of the total cross section for radiation produced by impact of 100-eV He^+ ions on Xe. While cascading effects must be assessed for each state on an individual basis, overall cascading contributions account for about 30% of the total observed radiation (visible and VUV) in the He^+/Xe reaction at 100-eV ion energies.

De Heer and co-workers[21] have extensively studied this system at impact energies above 300 eV. The highest ion energy attainable on our instrument is 150 eV preventing a *direct* comparison with the data of De Heer and co-workers.[20,21] Nevertheless, one might expect many similarities in the results of these two studies; however, some gross disparities exist in the states populated and in their total emission cross sections. De Heer and co-workers[21] make no mention of transitions from $6s\ ^4P_{1/2}$, $5d\ ^4P_{1/2}$, or $5d\ ^2P_{1/2}$ levels. It is presumed, therefore, that transitions from these three levels are relatively unimportant under their experimental conditions, although these are the three most intense lines observed in the present study. No XeI resonance lines were observed in this investigation, yet De Heer and co-workers report large apparent emission cross sections for XeI resonance lines ($\sigma > 0.15$ Å^2 at 147 nm).

While a detailed comparison of the experimental methods of De Heer *et al.*[20,21] with those of the present study will not be presented here, it is appropriate to note some obvious differences which may account for this discrepancy. One important difference is the ion beam flux. De Heer *et al.* used a plasma ion source which resulted in a much larger flux of He^+ ions in the collision region than is realized in the present experiments (typically larger by a factor of 10^5). This very large density of He^+ ions may permit the occurrence of neutral-neutral excitation processes in the collision region. De Heer *et al.*[21] find that the cross sections for the resonance atomic lines do not vary linearly with pressure in the collision region. This indicates that some of the radiative states may be formed by competitive processes in their experiments, and these authors suggest that fast He atoms may be involved. In the experiments reported here, the cross sections of all major emissions were found to depend linearly upon collision chamber pressure, up to pressures of 8 mTorr. These emissions therefore result only from bimolecular He^+/Xe reactions with little possibility of their formation by He-atom reactions or other processes.

It is noteworthy that Tanaka *et al.*[22] have recently observed a strong emission line of XeII, corresponding to the transition $5p^5\ ^2P^o_{3/2} - 6s\ ^4P_{1/2}$, from the excitation of a mixture of He and Xe in an ac pulsed discharge at a total pressure of about 10 Torr. As shown in Tables II and III, this line is one of the major emissions observed in the present study. Tanaka *et al.*[22] detected only very weak emission bands from the $(HeXe)^+$ diatomic ion.

The results of the present investigation indicate that the production of radiative states of XeII in the reaction of He^+ (100 eV, lab) with Xe is quite efficient. The total cross section for direct excitation measured in this study consitutes about 25% of the total He^+/Xe charge-transfer cross section (10 Å^2 at 100 eV).[23] A complete reporting of all lines observed in this and other He^+ rare gas systems is in preparation.

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