

## Inelastic processes leading to excited-state formation in He<sup>+</sup> and H<sup>+</sup> collisions with Na and K

G. H. Bearman, S. D. Alspach, and J. J. Leventhal

*Department of Physics, University of Missouri at Saint Louis, Saint Louis, Missouri 63121*

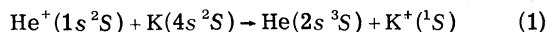
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Energy partitioning among accessible product excited states has been spectroscopically studied in a beam apparatus for He<sup>+</sup> and H<sup>+</sup> collisions with Na and K atoms in the kinetic energy range 10–800 eV. The dominant observable inelastic channel in all collision systems was found to be collision-induced excitation yielding resonance radiation. While excited states of K<sup>+</sup> formed by charge exchange were also observed, no analogous Na<sup>+</sup> emissions were detected; the absence of Na<sup>+</sup> emissions is attributed to inefficient energy conversion. Comparison of data from one-electron and two-electron processes supports the propensity rule which states that the former are generally favored.

### I. INTRODUCTION

Excited-state production in ion-atom or ion-molecule collisions may be studied by spectral analysis of radiation emitted by product species. Although a variety of inelastic channels, such as reactive scattering<sup>1–3</sup> and collision-induced excitation<sup>4,5</sup> (CIE), have been observed using this technique, it has been found that charge-transfer excitation (CTE) processes frequently dominate. This dominance of CTE may in part be attributed to reaction energetics of the systems studied which often favor CTE over CIE. In an effort to better understand the partitioning of energy among final states we have performed experiments with target sodium and potassium atoms. Since neutral alkali-metal atoms have low-lying excited states, CIE processes may compete favorably with CTE. Furthermore, since many excited states of both the neutral alkali-metal atom and the alkali-metal ion radiate within our detectable wavelength range (200–850 nm), competition between these channels may be studied. In addition to the intrinsic interest in these collisions the study of H<sup>+</sup>–alkali-metal-vapor interactions is relevant to plasma diagnostics.<sup>6</sup>

The low ionization potential of alkali-metal atoms makes these species attractive as electron donors in CTE processes designed to yield metastable rare-gas atoms. For example, the reaction



is exothermic by about 0.4 eV, so that He<sup>+</sup>–K collisions may be expected to efficiently produce metastable helium atoms. However, if a competing process, such as CIE, has a high cross section then the efficiency of reaction (1) for production of metastable helium atoms would suffer. Results to be presented in this paper show that CIE cross sections in collisions between He<sup>+</sup> or H<sup>+</sup> and Na or K are indeed high enough to effectively com-

pete with other inelastic channels.

Previous studies from our laboratory<sup>7,8</sup> have shown that collisions in which only one electron is promoted or removed are favored over those in which two electrons are involved. This “propensity rule” seems to play a more important role than reaction energetics in determining the preferred inelastic channels. For example, although the Cd<sup>+</sup> ion has a variety of radiating energy levels that could be produced in nearly thermoneutral He<sup>+</sup>–Cd collisions, the preferred exit channel is exothermic by about 7 eV.<sup>8</sup> The Cd<sup>+</sup> state produced in this preferred channel is one which is formed by removal of a 4*d* electron from the ground state ... (4*d*)<sup>10</sup> (5*s*)<sup>2</sup> configuration of neutral Cd. The Cd<sup>+</sup> states referred to above, for which He<sup>+</sup>–Cd collisions may be nearly resonant must be formed by removal of one 5*s* electron and promotion of the other—a two-electron process. The experiments reported here involving alkali-metal-atom targets provide another opportunity to investigate the relative importance of one- and two-electron processes. For alkali metals, excited states of the neutral atom are formed by promotion of the outer *s* electron, while almost all ionic states result from two-electron processes.

### II. EXPERIMENTAL

Ions are formed in an electron-impact ion source and focused into a beam with a set of cylindrical electrostatic lenses. After magnetic mass selection the beam is accelerated or decelerated to the desired collision energy with another set of cylindrical electrostatic lenses and focused into a collision cell which is mounted on top of the alkali-metal oven.

Although the vapor pressure in the collision cell was not independently determined, comparison of our data to the absolute emission cross sections for He<sup>+</sup>–K reported by Salop *et al.*<sup>9</sup> indicates that

the pressure of potassium vapor in the collision cell was about 0.2 mtorr; by comparing the potassium- and sodium-vapor-pressure curves the sodium-vapor pressure is estimated to have roughly the same value. At these low target-atom densities only single-collision processes should occur. Assuming total charge-transfer cross sections<sup>6,10</sup> as high as  $100 \text{ \AA}^2$ , the mean free path of an ion through the vapor is  $\sim 10$  times the collision path length. In addition, the ion beam was not attenuated when the oven was heated, suggesting low alkali-atom densities.

A Faraday cup behind the collision cell is used to monitor the ion current with an electrometer. A slot in the side of the collision chamber allows photons to exit and pass through a quartz window in the vacuum-chamber wall and enter a  $\frac{1}{4}$ -m scanning monochromator with entrance slit oriented parallel to the ion beam. Photons are counted with a cooled photomultiplier having a usable wavelength range 200–850 nm. Emission spectra are assembled by stepping the monochromator through the wavelength region of interest and counting photons at each wavelength setting. Repetitive scans are employed for signal averaging. A PDP-8E computer controls the monochromator, stores the data, and samples the ion-beam current. The computer is also used to correct the data for the relative spectral response of the optical system, obtained from standard lamps and branching ratios.

### III. RESULTS

Figure 1 shows a spectrum resulting from 100-eV (lab)  $\text{He}^+$ -K collisions. Most features are KI

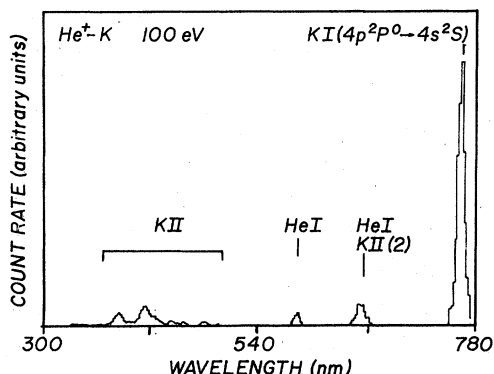


FIG. 1. Emission spectrum (300–780 nm) from 100-eV (lab)  $\text{He}^+$ -K collisions. The photon signal has been corrected for the relative spectral efficiency; the spectral resolution was 8 nm (full width at half maximum). The He I line at 667.8 nm appears larger than it is, due to a second-order contribution of a K II line; this is indicated by K II(2).

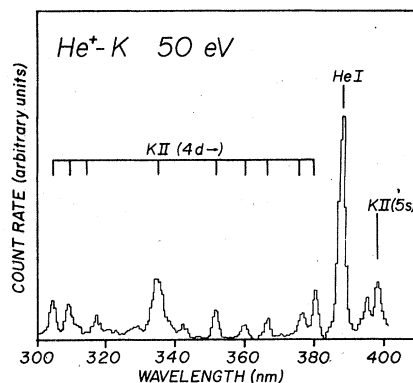


FIG. 2. Emission spectrum (300–400 nm) from 50-eV (lab)  $\text{He}^+$ -K collisions. The photon signal has been corrected for the relative spectral efficiency; the spectral resolution was 1 nm FWHM. The indicated electronic configurations are those of the upper states of the observed lines of K II.

and K II lines which result from either CTE or CIE. The KI resonance line is the strongest line in the spectrum. Two higher-resolution spectra are shown in Figs. 2 and 3. These spectra contain a few He I lines as well as KI lines. The lifetimes of the observed KI<sup>11</sup> and KII<sup>12</sup> states are about 10 ns, so that in these experiments all upper states leading to observed lines decay before the excited atom moves out of the field of view of the optical system.<sup>1</sup> Only one transition was observed that could populate the upper state of the KI resonance line (the 693-nm KI line); because this line is weak, the KI resonance doublet is considered to be cascade free. At these collisional energies

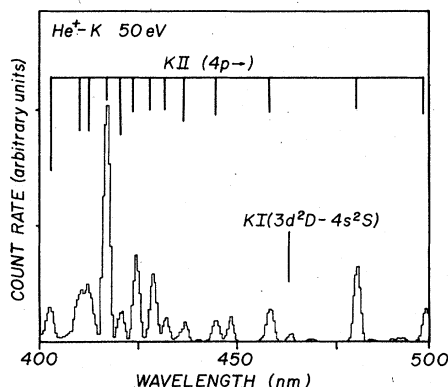


FIG. 3. Emission spectrum (400–500 nm) from 50-eV (lab)  $\text{He}^+$ -K collisions. The photon signal has been corrected for relative spectral efficiency; the spectral resolution was 1 nm FWHM. All the K II states observed in emission in this wavelength region originate from the K II ( $3p^54p$ ) configuration, as indicated.

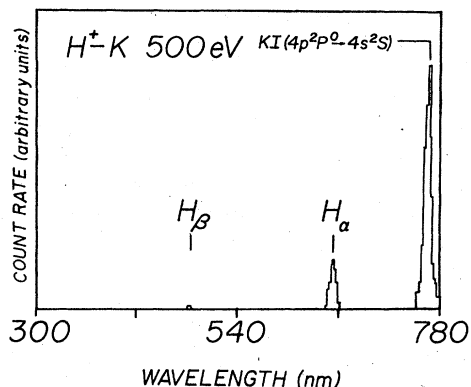


FIG. 4. Emission spectrum (300–780 nm) from 500-eV (lab)  $H^+ - K$  collisions. The photon signal has been corrected for the relative spectral efficiency; the spectral resolution was 5 nm FWHM. A greatly expanded signal scale in the region 300–500 nm reveals no  $K II$  lines.

(10–800 eV), the upper states of the  $K I$  resonance doublet ( $4p^2P_{1/2}$  and  $4p^2P_{3/2}$ ) were statistically populated; that is 1:2.

$H^+ - K$  collisions yielded only Balmer emissions and  $K I$  resonance radiation at all energies. Figure 4 is typical of  $H^+ - K$  collision-produced spectra. These data differ from the  $He^+ - K$  results in that no  $K II$  excited states from  $H^+ - K$  collisions are observed at any kinetic energy.

By comparing a given  $K II$  line signal from  $He^+ - K$  collisions to the measured absolute emission cross section reported by Salop *et al.*<sup>9</sup> cross sections for other emissions may be assigned. This procedure yields  $\sigma(4s \rightarrow 4p) \approx 4 \text{ \AA}^2$  for 600-eV  $He^+ - K$  collisions and  $\sigma(4s \rightarrow 4p) \approx 1.3 \text{ \AA}^2$  for 600-eV  $He^+ - K$  collisions. The total emission cross section

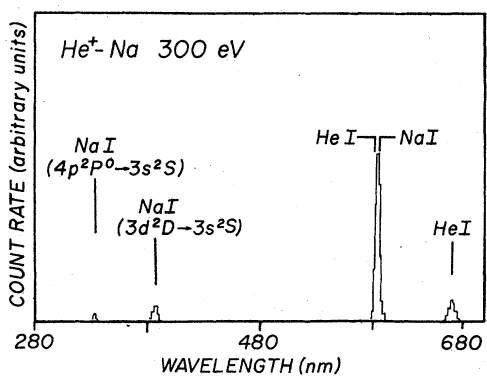


FIG. 5. Emission spectrum (280–680 nm) from 100-eV (lab)  $He^+ - Na$  collisions. The photon signal has been corrected for the relative spectral response; the resolution is insufficient to separate the  $Na D$  (589 nm) line from the 587.5-nm  $He I$  line.

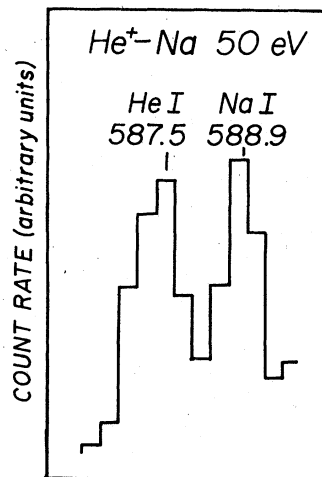


FIG. 6. Spectral scan of the wavelength region near the  $Na D$  line produced in 50-eV (lab)  $He^+ - Na$  collisions; the spectral resolution was 1 nm FWHM. The two lines are the 587.5-nm  $He I (3d^3D \rightarrow 2p^3P^0)$  transition and the unresolved  $Na D$  doublet (588.9 and 589.6 nm).

for all observed  $K II$  emissions from  $He^+ - K$  collisions is comparable to  $\sigma(4s - 4p)$ .

Data were also acquired for  $He^+$  and  $H^+$  collisions with sodium; the results of these experiments were substantially different from the potassium studies. Figure 5 shows a collision-produced spectrum from 300-eV (lab)  $He^+ - Na$  collisions. No  $Na II$  lines were observed with either  $He^+$  or  $H^+$  as projectiles at any kinetic energy. As was the case for potassium, the  $D$  line resulting from CIE was the prominent spectral feature for both  $He^+$  and  $H^+$  impact. However, for  $He^+$  collisions, charge transfer yielding excited neutral-helium atoms was comparable to CIE, in contrast to the  $He^+ - K$  system. The higher-resolution data in Fig. 6 show that the  $He I$  line at 587.5 nm is almost as strong as the  $D$  lines at 588.9 and 589.6 nm. The only other spectral features result from CIE processes yielding other excited  $Na I$  states.  $H^+ - Na$  produced only Balmer emissions and resonance lines, as was the case for  $H^+ - K$  collisions. For  $H^+$  impact on both  $Na$  and  $K$ , the  $H_\alpha$  Balmer line signal was always less than one-fourth of the resonance line signal.

#### IV. DISCUSSION

The processes observed in this study can be conveniently classified as either one-electron (1- $e$ ) or two-electron (2- $e$ ) processes. One-electron processes involve promotion or removal of a single electron, and include charge transfer (with excited neutralized ion), CIE, and collisional ionization. Two-electron processes observed here in-

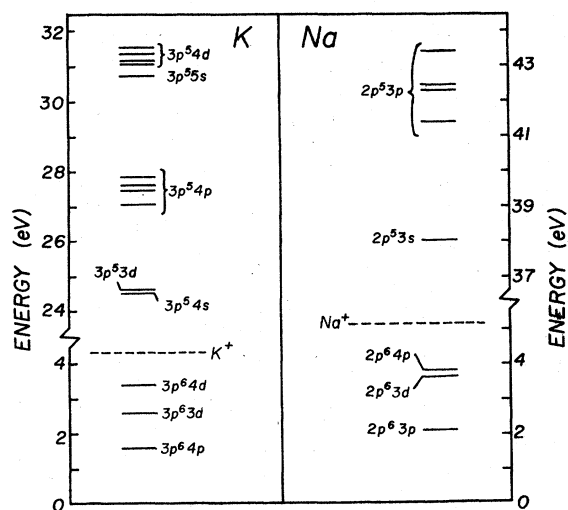


FIG. 7. Some relevant electronic states of NaI, NaII, KI, and K II. Note that the ordinates are different for Na and K. The electronic configurations are given for these states; energies are measured from the ground state of the neutral atom. Several ionic states may originate from the same electronic configuration, as indicated.

involve simultaneous promotion of one electron and removal of another. All but two of the singly charged alkali-ion states (lying below the doubly charged continuum) must be formed by 2- $e$  processes in these experiments. Figure 7 shows electron configurations and energies of some relevant Na and K states. The KI ground state is  $3p^6 4s^2 S$  and the known excited states of KI are formed by promotion of the 4s electron to 4p, 4d, 5s, etc. Only the ground state of K II ( $3p^6$ ) and the first excited state ( $3p^5 4s$ ) may be formed in a 1- $e$  process; production of all the other states, which have  $3p^5(nl)$  configurations, requires 2- $e$  processes. Na has analogous electronic structure; the Na I ground state is  $2p^6 3s^2 S$ , while the Na II excited states are  $2p^5(nl)$ .

Although  $\text{He}^+$ -K collisions yielded product K II states (in 2- $e$  processes) no analogous Na II states were observed in  $\text{He}^+$ -Na collisions. In assessing the relative importance of 1- $e$  and 2- $e$  processes the consequences of undetectable products must be considered. Table I lists  $Q$  values for some possible product states together with entries indicating detectability in our apparatus and the na-

TABLE I. Energetics for production of product states in collisions of  $\text{He}^+$  with Na and K.

Product <sup>a</sup>	$Q(\text{Na})^b$ (eV)	$Q(\text{K})^b$ (eV)	Type <sup>c</sup>	Detectable
He( $2s^1 S$ )	-1.18	-0.38	1- $e$	No
He( $2s^3 S$ )	-0.38	+0.42	1- $e$	No
He( $2p^3 P^o$ )	-1.51	-0.71	1- $e$	No
He( $3p^3 P^o$ )	-3.56	-2.76	1- $e$	Yes
He( $4p^3 P^o$ )	-4.26	-3.46	1- $e$	Yes
He( $3d^3 D$ )	-3.62	-2.82	1- $e$	Yes
He( $2p^1 P^o$ )	-1.77	-0.97	1- $e$	No
He( $3p^1 P^o$ )	-3.64	-2.84	1- $e$	Yes
He( $3d^1 D$ )	-3.62	-2.82	1- $e$	Yes
$\text{K}^+(^1 S)^d$		+20.26	1- $e$	No
$\text{K}^+(4s[1\frac{1}{2}]^o)$		+0.11	1- $e$	No
$\text{K}^+(4p[1\frac{1}{2}]^1)$		-3.0	2- $e$	Yes
$\text{K}^+(4p[1\frac{1}{2}]^0)$		-3.27	2- $e$	Yes
$\text{K}^+(3d[1\frac{1}{2}]^o)$		0	2- $e$	No
$\text{K}^+(5s[1\frac{1}{2}]^o)$		-6.1	2- $e$	No
$\text{Na}^+(^1 S)$	+19.46		1- $e$	No
$\text{Na}^+(3s[1\frac{1}{2}]^o)$	-13.3		1- $e$	No
$\text{Na}^+(3p[1\frac{1}{2}]^1)$	-16.9		2- $e$	Yes

<sup>a</sup> Product alkali-metal ion in the ground state.

<sup>b</sup>  $Q > 0$  corresponds to an exothermic process.

<sup>c</sup> 1- $e$  is a one-electron process; 2- $e$  refers to a two-electron process.

<sup>d</sup> He neutral in ground state.

ture of the process (1- $e$  or 2- $e$ ). Clearly there are a large number of unobservable 1- $e$  exit channels that might reasonably be expected to occur. Olson and Smith<sup>13</sup> have calculated partial charge-transfer cross sections for He<sup>+</sup>-K collisions in the range 10–1500 eV. They conclude that the 1- $e$  processes yielding the  $2p^1P$ ,  $2p^3P$ ,  $2s^1S$ , and  $2s^3S$  states of He I comprise virtually the entire measured total charge-transfer cross section.<sup>10</sup> Since these total charge-transfer cross sections are large ( $\sim 80 \text{ \AA}^2$  at 600 eV), and we observe relatively low yields ( $\sim 4 \text{ \AA}^2$  at 600 eV) of excited K II, formation of substantial amounts of undetected He I must occur. Therefore 1- $e$  processes probably dominate in this energy range.

It is possible that some K II excited states are produced by Auger transitions from autoionizing KI states formed in 1- $e$  CIE processes. Although a large number of KI autoionizing states are known,<sup>14</sup> it has been shown that they autoionize to the K II ground state.<sup>14,15</sup>

The dominance of the alkali resonance lines in these collision systems demonstrates the ease of excitation of the outer electron in collisions with ions. Additional experiments were performed using neutral H- and He-atom beams as projectiles with both Na and K as targets. In these systems, CIE resulting in neutral H or He lines was observed, but the only alkali emissions were the resonance lines, which again dominated. Studies<sup>16–18</sup> with low-energy alkali-metal beams (1–50 eV) have shown that cross sections for CIE to the first excited state are greater than  $1 \text{ \AA}^2$  down to within a few electron volts of threshold. These large CIE cross sections involve promotion of the single outer-shell electron. Similarly, high CIE cross sections have been observed in studies of Be<sup>+</sup> and Mg<sup>+</sup> collisions with rare gases.<sup>19,20</sup> These latter systems have also been studied theoretically.<sup>21</sup>

In order to produce the observed 2- $e$  states of K II, one electron must be removed and another promoted to yield a  $3p^5(nl)$  configuration. The ease with which the 4s electron is promoted, as evidenced by the present CIE results, suggests a possible mechanism for the 2- $e$  CTE production of

$3p^5(nl)$  K II states. This mechanism involves promotion of the 4s electron and removal of a  $3p$  electron. Comparison of the observed higher-lying KI states with the observed K II states provides support for the possibility that this is the operative mechanism. These other KI states have  $3p^64p$ ,  $3p^64d$ , and  $3p^63d$  configurations. The strongest observed K II lines originate from the  $3p^54p$  configurations, while weaker lines are observed from the  $3p^54d$  configuration. The only difference between these KI and K II states is a  $3p$  electron, suggesting that the 4s electron is collisionally promoted to ( $nl$ ), while a  $3p$  electron is removed to form excited K II. Therefore, if indeed this is the mechanism, these 2- $e$  CTE channels and the observed CIE may be envisioned as resulting from similar collisions; the difference depends on whether or not an inner ( $3p$ ) electron is removed. While we observe a  $3p^63d$  KI state from CIE, the analogous K II state ( $3p^53d$ ) radiates at 60.7 nm and cannot be detected in these experiments. A  $3p^55s$  K II state is observed, but the corresponding  $3p^65s$  KI state radiates at 1240 nm so that these two states cannot be correlated.

In contrast to the He<sup>+</sup>-K system no alkali-metal-ion lines are observed from He<sup>+</sup>-Na collisions. In order to produce the first detectable states of Na II (the  $2p^53p$  multiplet), 17 eV must be converted from kinetic energy to internal energy in the collision. This is considerably more than for the analogous He<sup>+</sup>-K processes where  $\sim 3$ –4 eV must be converted. The absence of Na II lines at energies up to 1.3 keV indicates that the conversion efficiency of kinetic to internal energy is insufficient in these collisions to form Na II excited states. On the other hand, for potassium targets, sufficient kinetic energy is converted to overcome the relatively smaller energy deficit.

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