Observation of Two-Electron Penning Ionization in a Thermal-Energy Collision

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The existence of the hybrid Penning reaction, $\mathrm{He}^+ + X \rightarrow \mathrm{He} + X^{++} + e$, has been confirmed for thermal-energy collisions of He^+ with Mg, Ca, Sr, Ba, Y, Ce, Yb, Sn, and Pb. A new two-electron Penning reaction, $\mathrm{He}^* + X \rightarrow \mathrm{He} + X^{++} + 2e$, has been identified in He*-Ce and He*-Y collisions.

Penning ionization[1] is customarily defined as a second-kind collision of the form

$$A^* + B \rightarrow A + B^+ + e. \tag{1}$$

This type of collision is always accompanied by the ejection of an electron and by a net decrease in the total internal energy of the constituents. Using a flowing afterglow system, we have isolated nine cases of a hybrid Penning ionization process,

$$\mathrm{He}^+ + X \rightarrow \mathrm{He} + X^{++} + e, \tag{2}$$

consisting of both ionization and charge transfer. In two instances, a two-electron Penning ionization process,

$$\mathrm{He}^* + X \rightarrow \mathrm{He} + X^{++} + 2e, \tag{3}$$

has also been identified which exhibits a radically different reaction selectivity from that displayed by (1) and (2). The peculiar selectivity of two-electron Penning ionization may explain why this process has eluded identification in previous studies of thermal energy collisions involving helium metastable atoms.

At the collision energies available in beam experiments, (2) may proceed as a collision of the first kind. The reaction is then termed ionization and capture[2] and is accompanied by a net increase in total internal energy. In recent studies of these collisions, Maier[3] has observed that the threshold energy typically occurs some 0–4 eV above the point at which the reaction becomes energetically possible. By contrast, no significant collision energy should be required in order to initiate hybrid Penning ionization. Green[4] has proposed that (2) may be responsible for the thermal-energy X^{++} ion formation he observed in flowing afterglow experiments with Ca and Pb. The present flowing afterglow measurements confirm the existence of the hybrid Penning process and in addition establish the existence of a new two-electron Penning reaction.

Flowing afterglow methods[5-7] provide some special advantages over pulsed afterglow techniques[8-10] for the study of relative collision cross sections. A flowing afterglow system displays a discharge with a spatial decay pattern which maintains a one-to-one correspondence with the temporal decay pattern of an equivalent pulsed discharge. In the pulsed system a given point in time can only be sampled periodically, whereas in the flowing system the equivalent temporal point may be examined continuously. This advantage is illustrated in the experimental arrangement presented in Fig. 1. The material to be examined is evaporated into the afterglow at a preselected point in equivalent time. A mass-spectroscopic analysis of the resultant ions may then be continuously conducted at another and later point in equivalent time. A second advantage of flowing afterglows is that materials with evaporation temperatures as high as 2000°K may be introduced into the reaction region. Thirdly, flowing afterglows can provide an unusually intense source of thermalized $\mathrm{He}(2^3S)$ metastable atoms and $\mathrm{He}^+(^2S_{1/2})$ ions; moreover, these species can be generated in a variable ratio. Optical and microwave absorption measurements in the reaction region of Fig. 1 indicate attainable $\mathrm{He}(2^3S)$ and $\mathrm{He}^+(^2S_{1/2})$ densities of 5×10^{10} and 10^{12} cm^{-3}, respectively.

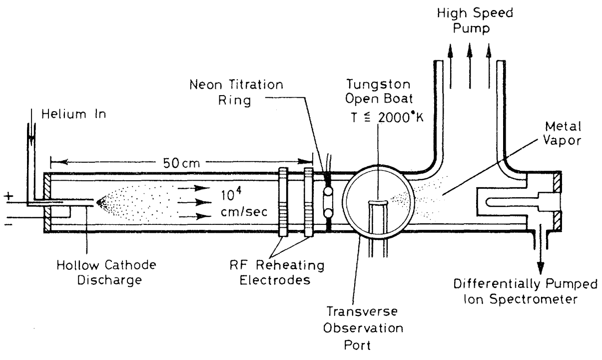

FIG. 1. Flowing afterglow apparatus with provision for optical and mass-spectroscopic diagnostics.

At low pressures, the densities of all excited helium states upstream of the reaction zone are relatively small with respect to He(2^3S) and He$^+$($^2S_{1/2}$) densities. Processes (2) and (3) can therefore be identified only with an ion mass spectrometer, provided a method of distinguishing between collisions involving He(2^3S) or He$^+$($2S_{1/2}$) is available. However, if helium resonance radiation generated in the discharge source region reaches the reaction zone, photoionization can produce doubly ionized reactant ions, X^{++}, thereby introducing interpretational errors. In addition, ordinary charge transfer or Penning ionization into levels just below the second ionization limit followed by stepwise electron-atom or atom-atom collisions may produce X^{++} ions. Finally, hybrid or two-electron Penning ionization directly into levels of the reactant's third spectrum may also produce X^{++} ions.

In our experiments, neon titration and rf heating were successively applied in order to discriminate unambiguously between He(2^3S) and He$^+$($^2S_{1/2}$) collision processes. These discriminants also provided a check on the presence of photoionization effects. When properly adjusted, the neon discriminant reduces the He(2^3S) population through resonant transfer collisions[10] without significantly affecting either the local He$^+$($^2S_{1/2}$) population or the upstream generation of resonance radiation. Any coupling between the He(2^3S) and He$^+$($^2S_{1/2}$) states due to metastable-metastable ionizing collisions[8] may be minimized by generating the majority of He$^+$($^2S_{1/2}$) states independently of local metastable pair ionization processes. Similarly, the rf discriminant may be adjusted to reduce selectively the He$^+$($^2S_{1/2}$) population by increasing the local ambipolar diffusion rate.[11] Coupling between the He(2^3S) and He$^+$($^2S_{1/2}$) states may again be minimized by generating the majority of He(2^3S) states independently of local recombination processes. The plasma conditions governing generation of the He(2^3S) and He$^+$($^2S_{1/2}$) populations and the adjustment of the two discriminants were regulated by monitoring charge transfer and Penning-excited lines in the spectrum of Zn II. For example, the emission at 6102 Å is known to be proportional to the He$^+$($^2S_{1/2}$) but not to the He(2^3S) population.[6,12] The converse holds for 5894-Å emission.[12] As an additional method for discriminating between He(2^3S) and He$^+$($^2S_{1/2}$) collision processes, the ratio of the He(2^3S) to the He$^+$($^2S_{1/2}$) populations in the reaction zone was varied from 1:20 to 1:1 by altering the discharge source current. In another set of tests, the possible existence of stepwise ionization processes was examined by observing the pressure and current dependence of the X^{++} ions. Last of all, direct production of excited X^{++} states was investigated spectroscopically.

TABLE I. Observation of X^{++} Penning processes. HP, hybrid Penning; TEP, two-electron Penning. The $4f5d6s^2$ configuration of Ce has been abbreviated.

Element	Electron configuration	Total IP^{++} (eV)	Effects observed
Mg	$3s^2$	22.7	HP
Ca	$4s^2$	18.0	HP
Sr	$5s^2$	16.7	HP
Ba	$6s^2$	15.2	HP
Y	$4d\,5s^2$	18.6	HP, TEP
Ce	$5d\,6s^2$	16.5	HP, TEP
Yb	$4f^{14}\,6s^2$	18.4	HP
Sn	$5s^2\,5p^2$	22.0	HP
Pb	$6s^2\,6p^2$	22.5	HP

The preceding tests were applied to the nine elements in Table I. For helium pressures in the range 300 to 500 μm, no formation of X^{++} ions as a result of either resonance radiation or stepwise ionization was detected. In two cases, Yb and Ce, direct excitation of the third spectrum is energetically possible; nonetheless, no photon emission from the third spectrum was observed. However, X^{++} ion formation due to hybrid Penning ionization was readily detectable in all nine elements with the ion mass spectrometer. The recorded X^{++} densities were all of comparable magnitude and usually within a factor of 3 of the more numerous X^+ densities. This seeming lack of selectivity for the rather complex hybrid reaction is also typical of ordinary Penning reactions. In sharp contrast to this behavior, two-electron Penning ionization was only detectable in Y and Ce, yet the process is also energetically possible in Ca, Sr, Ba, and Yb. Table I suggests that the apparent selectivity is associated with those elements possessing an outer d-electron ground-state configuration. In Ce, the magnitudes of the cross sections for hybrid and two-electron Penning ionization were found to be comparable. The two-electron process, however, is noticeably stronger in Ce than in Y and may be influenced by the He(2^3S)-X^{++} energy defect.[13]

Energy-defect arguments also favor the two-electron Penning ionization of Ba over Ce, but in this situation the ground-state configurations may well be the dominant factor. Figure 2 pre-

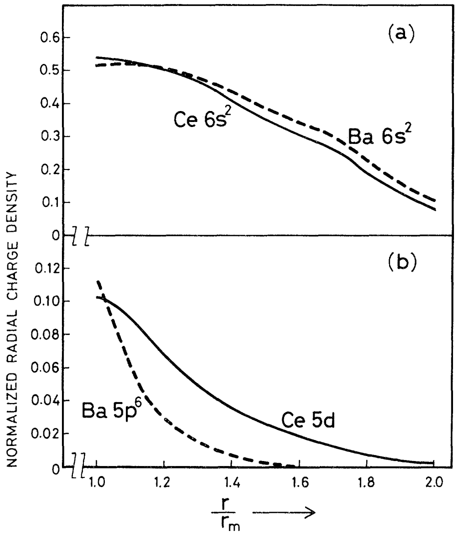

FIG. 2. Comparison of the radial charge densities $|rR|^2$ for the two outermost subshells of Ba and Ce.

sents a plot of self-consistent-field calculations[14] for the ground-state radial charge densities of the outer two subshells of both Ba ($Z = 58$) and Ce ($Z = 59$). The $5d$ charge density in Ce extends appreciably through the $6s$ subshell, whereas the $5p$ charge density in Ba does not. Although there are two electrons with antiparallel spins present in the $6s$ subshell of both elements, we have observed that two-electron Penning ionization is noticeably absent for Ba. A similar situation holds when Sr and Y are compared. In each of these comparisons, the presence of a third electron from the d subshell appears to play an important role in promoting two-electron Penning ionization. Investigations into the possible role of spin effects in the two-electron reaction are currently in progress.

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