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Use of polarization techniques to investigate the dynamics of Penning ionization reactions

L. G. Gray, R. S. Keiffer,* J. M. Ratliff, F. B. Dunning, and G. K. Walters
Department of Physics and The Rice Quantum Institute, Rice University, Houston, Texas 77251

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A new technique is used to probe the dynamics of Penning ionization reactions involving He(2^3S) atoms and the targets K, Rb, Cs, O_2, Cl_2, and CF_3Cl. In this technique, the electrons on the 2^3S atoms are spin labeled and the polarization of the Penning electrons is determined. The data indicate that, for Rb, a significant fraction of the ionization occurs through energy transfer to a core excited state followed by autoionization. The data for the molecular targets confirm that ionization via ionic channels is important.

Penning ionization reactions of the type

$$\mathrm{He}(2^3S)+X\rightarrow\mathrm{He}(1^1S)+X^{+}+e^{-}\ , \qquad (1)$$

where X may be an atom or molecule, have been the subject of numerous investigations. A wealth of information concerning reaction cross sections and energy distributions of the ejected electrons has been accumulated.[1] Although information concerning the dynamics of Penning ionization can be extracted from analysis of electron energy distributions,[1–5] many interesting questions remain. In the present paper we describe a novel method for probing the dynamics of Penning processes and, in particular, the origin of the ejected electron, i.e., whether it originates on the 2^3S atom or the target particle. In this approach the electrons on the He(2^3S) atoms are spin labeled, and the polarization of the ejected electrons is determined. Here we report the results of an exploratory study of Penning reactions involving alkali-metal atoms and several molecular gases that demonstrate the potential of this technique. The alkali metals are of interest because the measured Penning ionization cross sections[6] for Na and Cs are significantly lower than those for K and, especially, Rb, which has lead to speculation that there are additional channels through which ionization can occur in the latter cases. The molecular targets selected are ones for which electron energy distribution measurements suggest that ionic channels play an important role in Penning reactions.[3,4]

The present apparatus, described in detail elsewhere,[7–9] is shown schematically in Fig. 1. Briefly, a microwave discharge is used to generate He(2^3S) atoms in a flowing helium afterglow apparatus. The 2^3S atoms are optically pumped using circularly polarized 1.08-μm $2^3S\leftrightarrow 2^3P$ radiation to preferentially populate either the M_J $(M_S)=+1$ or -1 state.[10] Alkali-metal vapor, or a target gas, is then introduced into the afterglow leading to Penning reactions. The resultant electrons are extracted from the afterglow through a differentially pumped aperture and formed into a collimated beam by a series of electron lenses. The polarization of the extracted electrons is measured using a Mott polarimeter.[11]

A microwave discharge is used to excite the helium as it enters the flow tube through a nozzle. This excitation technique was adopted because it provides a low singlet (2^1S) to triplet (2^3S) metastable ratio ($\sim$1:10) in the after-

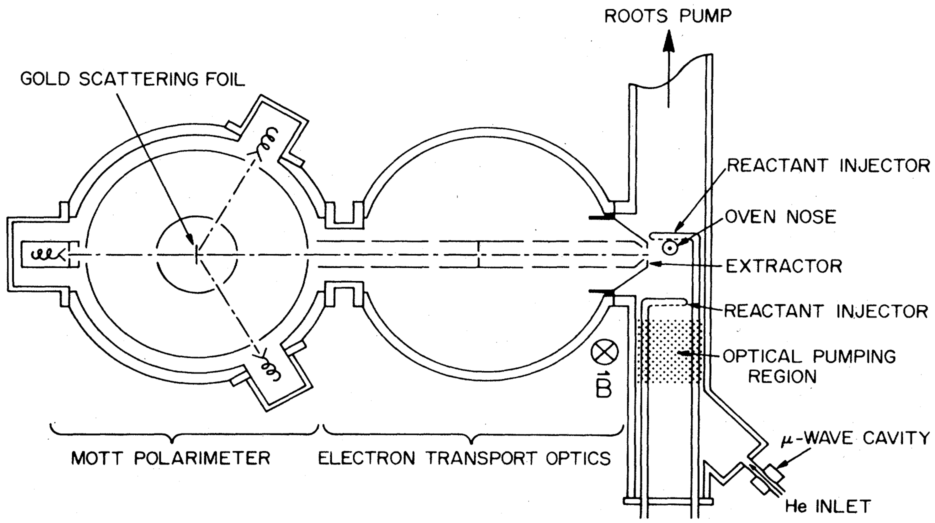

FIG. 1. Schematic diagram of the apparatus.

glow. Electrons and ions produced in the discharge diffuse rapidly to the walls of the flow tube where they recombine. For the present source-extractor separation these electrons do not contribute significantly to the extracted current.

The 2^3S atoms are optically oriented by absorption of circularly polarized 1.08-μm $2^3S \leftrightarrow 2^3P$ radiation from a high-power, rf-excited helium lamp, with subsequent decay to the 2^3S level by spontaneous emission.[10] The optical pumping radiation is incident parallel to a weak ($\sim$1 G) external magnetic field, transverse to the flow tube, that preserves a well-defined quantization axis. This field is generated using a series of magnetic field coils.

Alkali-metal vapor or target gas is injected immediately downstream of the electron extraction aperture. The 2^3S atoms are deexcited close to the extraction aperture by backstreaming vapor or gas. The alkali vapor is introduced using an oven equipped with a long, thin heated nose that extends into the flow tube. Gaseous targets are introduced using a ring injector (labeled 1 in Fig. 1).

The polarization of the 2^3S atoms following optical pumping is determined by injecting argon into the flow tube and measuring the polarization of the resultant Penning electrons. Penning reactions involving argon, a spin singlet, are known to conserve spin.[7,12] This results because the reaction can only proceed via the so-called exchange mechanism, in which an electron of appropriate spin from the target tunnels into the core hole of the 2^3S atom with simultaneous ejection of the 2*s* electron. The Penning reaction may be written

$$\mathrm{He}(2^3S)\{\uparrow\uparrow\}+\mathrm{Ar}(^1S_0)\{\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\} \rightarrow \mathrm{He}(1^1S)\{\uparrow\downarrow\}+\mathrm{Ar}^+(^2P_{1/2,3/2})\{\uparrow\downarrow\uparrow\downarrow\uparrow\}+e^-\{\uparrow\}\ . \tag{2}$$

The collision times are far too short to allow exit channel magnetic interactions to significantly influence the electronic spin states. Thus the polarization of the ejected electrons[13] reflects the initial polarization of the metastable atoms,[14] typically ~30%.

The target species of interest here have open valence shells, and most are not spin singlets. Thus the polarization of the electrons produced in Penning reactions may be degraded prior to extraction from the flow tube through spin-exchange reactions with other target atoms, typified by

$$e^-\{\uparrow\}+X\{\downarrow\}\rightarrow e^-\{\downarrow\}+X\{\uparrow\}\ . \tag{3}$$

To determine the importance of, and correct for, such effects, immediately following each polarization measurement, and without changing the target density, argon was introduced into the flow tube through a second injector (labeled 2 in Fig. 1) located upstream of the extraction aperture. The argon flow rate was sufficient to ionize all the 2^3S atoms in the immediate vicinity of this injector. In order to be extracted from the afterglow, these electrons, which initially have a polarization equal to the known 2^3S atom polarization, must pass through the target gas or vapor. Thus measurement of their polarization upon extraction reveals any degradation due to spin-exchange reactions and, in fact, affords a method for quantitatively determining rate constants for reaction (3) that we propose to exploit in the future. With the exception of O_2, spin-exchange effects were small for all the present target species. Following correction for spin-exchange effects, the Penning electron polarizations in all cases are observed to be independent of target density. Alternatively, measurement of the polarization as a function of target density permits correction for spin-exchange effects by simply extrapolating to zero target density. Data obtained using both techniques are in excellent agreement.

The polarizations of the electrons produced in Penning reactions involving K, Rb, and Cs, corrected for spin-exchange effects and normalized to a metastable atom polarization of 100%, are presented in Table I(a). Also included for reference are the corresponding Penning cross sections measured by Johnson *et al.*[6] In the case of Cs, the polarization of the ejected electrons is equal, within experimental error, to that of the 2^3S atoms. This indicates that Penning ionization proceeds via the simple exchange reaction,

$$\mathrm{He}(2^3S)\{\uparrow\uparrow\}+\mathrm{Cs}\{\downarrow\}\rightarrow \mathrm{He}(1^1S)\{\uparrow\downarrow\}+\mathrm{Cs}^+ + e^-\{\uparrow\}\ . \tag{4}$$

TABLE I. Polarization of electrons produced in Penning reactions with polarized He(2^3S) atoms, normalized to a 2^3S polarization of 100%.

Species	Electron polarization (%)	Penning cross section (Å^2)[6]
	(a) Alkali targets	
Na		33±6
K	93±7	55±10
Rb	71±9	93±18
Cs	100±5	34±7
	(b) Molecular targets	
O_2	31±5	
Cl_2	74±3	
CF_3Cl	90±4	

For Rb, however, the polarization of the ejected electrons is significantly lower than that of the 2^3S atoms. This requires that a fraction of the Penning reactions proceed by other than the exchange process. Such a mechanism was postulated by Johnson *et al.* to explain the anomalously large Rb Penning ionization cross section that they measured. They noted that Rb has a number of autoionizing levels that lie close in energy to the 2^3S level. They proposed that ionization might occur through excitation and subsequent autoionization of such states. (Such a process is not possible in the case of Cs as the corresponding autoionizing states do not lie close in energy to the 2^3S level.) Rubidium autoionizing levels have been investigated both spectroscopically and through electron impact.[15,16] The $4p^5 4d$ and $4p^5 5s$ core states cannot be treated separately due to strong configuration interaction. These states will be collectively referred to as $4p^5[4d\times 5s]$. The autoionizing states of interest in the present work thus have configurations $4p^5[4d\times 5s]nl$. The proposed reaction mechanism is illustrated by the schematic potential-energy diagram shown in Fig. 2. The attractive $^2\Sigma$ and repulsive $^4\Sigma$ interaction potentials for the incoming particles are shown by the upper curves. Measurements for other alkali-metals suggest that the depth of the $^2\Sigma$ potential will be ~ 0.5 eV.[2] The lower curve represents the interaction between the Rb^+ and $\mathrm{He}(1^1S)$ reaction products. Typical Rb^{**}-$\mathrm{H}(1^1S)$ interaction potentials are also included. These latter potentials are expected to be relatively flat because $\mathrm{He}(1^1S)$ is weakly interacting. In consequence, the $^2\Sigma$ potential curve will cross potential curves associated with a number of different autoionizing states, the transitions between these can lead to population of autoionizing levels through processes of the type

$$\mathrm{He}(2^3S)\{\uparrow\uparrow\}+\mathrm{Rb}(4p^6 5s)\{\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\ \downarrow\}$$
$$\rightarrow \mathrm{He}(1^1S)\{\uparrow\downarrow\}+\mathrm{Rb}^{**}(4p^5[4d\times 5s]nl)\{\uparrow\downarrow\uparrow\downarrow\uparrow\ \downarrow\ \uparrow\}\ . \tag{5}$$

If the lifetime against Rb^{**} autoionization is short compared to $\Delta t = \hbar/\Delta E_{\mathrm{s.o.}}$, where $\Delta E_{\mathrm{s.o.}}$ is the spin-orbit splitting of the $4p^5$ core, then the core vacancy can only be filled by the $[4d\times 5s]\{\downarrow\}$ electron leading to ejection of the $nl\{\uparrow\}$ electron, which has a polarization equal to that of the 2^3S atoms. However, the spin-orbit splitting of the core is quite large (~ 7380 cm^{-1}),[17] corresponding to $\Delta t \sim 10^{-15}$ sec. The lifetimes of the autoionizing levels can be estimated from the spectroscopic data[15] and are $\sim 10^{-13}$ to 10^{-14} sec. Thus spin polarization in the core can be lost to produce polarization of the orbital moment via the spin-orbit interaction prior to autoionization. Consideration of the appropriate Clebsch-Gordan coefficients shows that if the $4p^5$ core initially has, say, $M_s = +\frac{1}{2}$, then the subsequent time-averaged probability of the core having $M_s = +\frac{1}{2}$ $(-\frac{1}{2})$ is $\frac{19}{27}$ $(\frac{8}{27})$. Autoionization can then occur through either the $[4d\times 5s]$ or the nl electron decaying to fill the $4p$ subshell with simultaneous ejection of the other electron. Thus, as is observed, the polarization of the ejected electrons will be lower than that of the metastable atoms. If it is assumed that the autoionizing rates associated with decay of either the $[4d\times 5s]$ or nl electron to fill the $4p$ subshell are in direct proportion to the time-averaged probability that the core has the required M_s value, the present data would suggest that $\sim 48\%$ of the Penning reactions proceed via the autoionizing channel.

Johnson *et al.* postulated that Penning ionization via autoionizing channels might also occur for K. The present data provide indications that such a channel might be operative, but to a much lesser extent than for Rb. This is not surprising since only a few K autoionizing doublet states lie close in energy to the 2^3S level.[17,18]

The polarizations of the electrons resulting from Penning ionization of several molecular targets are shown in Table I(b). In each case the polarization of the ejected electrons is smaller than that of the metastable atoms, indicating that a fraction of the Penning reactions must proceed by other than the exchange channel. This supports the conclusions of Morgner and co-workers[3,4] based on measurements of the corresponding Penning electron energy distributions. These data provide evidence that, for each target M included in Table I(b), a significant fraction of the ionization occurs following a transition from the covalent $\mathrm{He}(2^3S)$-M entrance potential onto a strongly attractive He^+-M^- ionic potential. This ionic channel leads to a broad distribution of electron energies, superimposed on which are a number of discrete peaks resulting from ionization out of the covalent entrance channel. The present polarization data are entirely consistent with the existence of the ionic channel. However, energy-resolved polarization measurements will be required to directly investigate spin conservation during ionization via the ionic channel and to assess the relative

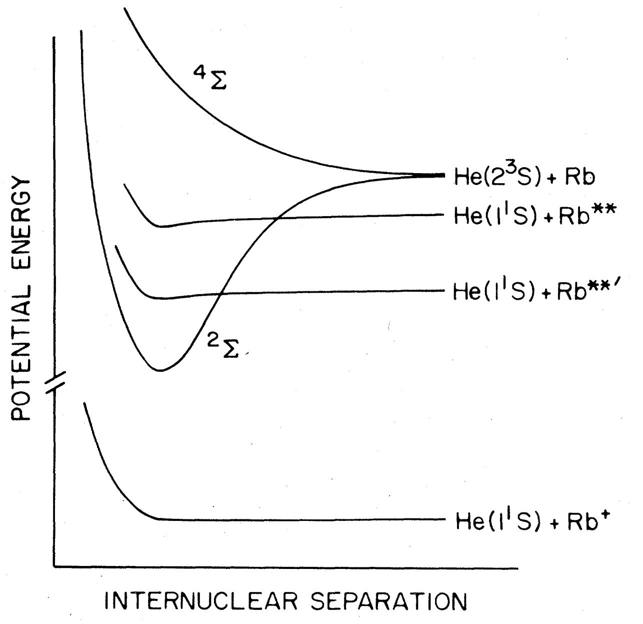

FIG. 2. Schematic diagram of the potential energy curves important in $\mathrm{He}(2^3S)$-Rb interactions.

importance of the ionic and covalent channels. Such measurements are feasible, it having been demonstrated that Penning electrons can be extracted without distorting the energy distribution characteristic of their production.[19] Although the apparatus is undergoing extensive modifications to permit energy-resolved polarization measurements, the present data demonstrate that the study of spin dependences in Penning reactions can provide much new information on the dynamics of such processes.

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[*] Present address: 523 Arabella Street, New Orleans, LA 70115.

[1] For a recent detailed review of Penning ionization, see A. J. Yencha, in *Electron Spectroscopy: Theory, Techniques and Applications,* edited by C. R. Brundle and A. D. Baker (Academic, New York, 1984), Vol. 5, pp. 197—373.

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[13] Defined as $(n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, where $n_\uparrow$ and $n_\downarrow$ are the number of electrons with spin "up" and "down" relative to the quantization axis.

[14] Defined as $(n_+ - n_-)/(n_+ + n_0 + n_-)$, where n_+, n_0 and n_- are the number of 2^3S atoms in the M_J $(M_S) = +1$, 0, and -1 levels, respectively.

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