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Use of spin-labeling techniques to study the dynamics of Penning-ionization reactions

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Spin-labeling techniques, specifically the use of electron-spin-polarized He($2\,^3S$) metastable atoms coupled with energy-resolved spin analysis of the product electrons, are used to investigate the dynamics of Penning ionization in collisions involving He($2\,^3S$) atoms. Results obtained using CO_2, CO, Cl_2, and O_2 target gases are presented that illustrate the capabilities of this approach. In particular, the data for Cl_2 and O_2 confirm that ionization via ionic channels is important and show that exchange and spin-orbit effects must be considered.

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In recent years there has been increasing interest in the dynamical processes governing Penning-ionization (PI) reactions of the type

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

involving He($2\,^3S$) metastable atoms and some atomic or molecular target $\mathcal{M}$ [1]. Analysis of energy distributions of product electrons using a potential-curve model shows that PI can frequently be described simply in terms of a direct transition from the covalent He($2\,^3S$)+$\mathcal{M}$ entrance potential to the final He($1\,^1S$)+$\mathcal{M}^+$ exit potential. Because neither potential is strongly dependent on internuclear separation, ionization via such a "covalent" channel results in a narrow distribution of Penning electron energies. For targets having a positive electron affinity, however, ionization may be preceded by an adiabatic transition from the covalent entrance potential onto a strongly attractive $\mathrm{He}^{+}+\mathcal{M}^{-}$ ionic potential. Because this potential changes rapidly with internuclear separation, ionization via this "ionic" channel leads to a broad distribution of electron energies. Here we demonstrate that spin-labeling techniques, specifically the use of electron-spin-polarized He($2\,^3S$) atoms coupled with energy-resolved spin analysis of the product electrons, can provide further insight into the dynamics of PI reactions. Data obtained with CO_2, CO, Cl_2, and O_2 target gases are presented which illustrate the potential of this approach and which show that, under certain conditions, exchange and spin-orbit effects can be important.

The present experiments are undertaken using the flowing afterglow apparatus shown schematically in Fig. 1 [2]. Briefly, a microwave discharge is used to generate He($2\,^3S$) atoms in a flowing helium afterglow which are optically pumped to populate preferentially either the $M_J(M_S)=+1$ or -1 magnetic sublevels. Target gas is then introduced into the afterglow, resulting in the production of free Penning electrons. A fraction of these electrons escape from the afterglow through a differentially pumped aperture, and their polarization is measured as a function of energy using a hemispherical energy analyzer and Mott polarimeter [3].

The afterglow is contained in a 10-cm-diam Pyrex flow tube that is exhausted by a high-speed Roots pump and is lined with copper sheet to minimize stray electric fields. Helium gas entering the flow tube is excited by a microwave discharge which produces predominantly He($2\,^3S$) atoms with negligible He($2\,^1S$) contamination. Electrons and ions produced in the discharge diffuse rapidly to the walls of the flow tube where they recombine. However, even for the present source-to-extraction-aperture separation of 80 cm, (unpolarized) source-produced electrons can, under certain conditions, provide a small contribution to the extracted electron current at energies $\lesssim 0.5$ eV and data are therefore not reported in this energy regime. The $2\,^3S$ atoms are optically oriented by absorption of circularly polarized 1.083-μm $2\,^3S_1\rightarrow 2\,^3P_1$ radiation from a single-mode, frequency-stabilized lanthanum neodymium magnesium hexaaluminate (LNA) laser [4] with subsequent spontaneous decay back to the $2\,^3S$ level. The laser beam is incident parallel to a weak ($\sim$0.2 G) magnetic field established transverse to the axis of the flow tube that provides a well-defined quantization axis. Target gas is injected into the flow tube close to the extraction aperture using a fine hypodermic needle. Tests showed that, with the exception of O_2, the measured electron energy distributions

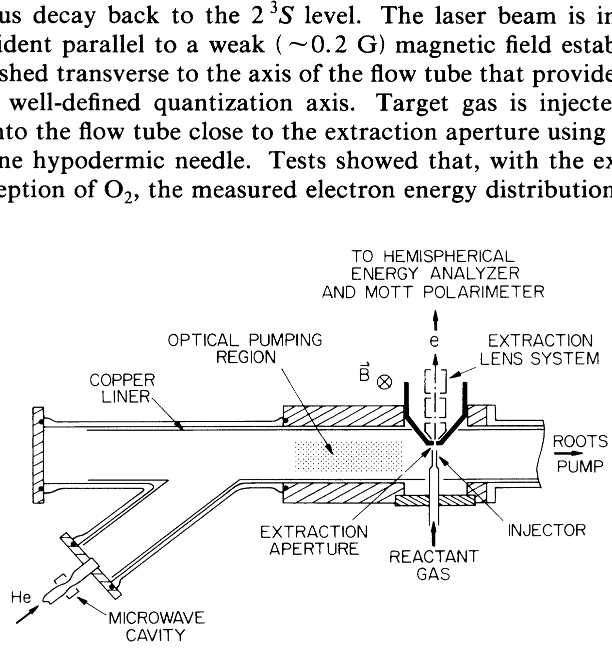

FIG. 1. Schematic diagram of the apparatus.

(EED's) and polarizations were insensitive to target-gas flow rate over a wide range. For O_2, low flow rates are used to ensure that the electron polarization is not degraded through exchange in e^--O_2 collisions [5].

Electrons produced in PI reactions diffuse to the walls of the flow tube, and those that pass through the extraction aperture are formed into a beam by a series of electrostatic lenses. The flow tube is operated under conditions [low He($2\,^3S$) and reactant densities, and hence low product-electron densities] such that electrons leave the afterglow under free diffusion conditions before their energies can be significantly changed by collisions. The extracted electrons are energy analyzed using a hemispherical analyzer whose energy resolution (~ 0.4 eV) was chosen to obtain relatively high transmitted electron currents (to facilitate polarization measurements) while providing sufficient discrimination to permit separate study of different features in the Penning-electron spectra. A compact retarding-potential Mott polarimeter operating at 20 kV is used to measure the electron polarization [3].

Prior to each data acquisition run, the polarization [6] P_z of the He($2\,^3S$) atoms was determined by admitting Ar to the flow tube and measuring the polarization of the resulting Penning electrons. Previous studies [7] have shown that PI reactions with Ar proceed directly through the covalent channel and that spin angular momentum is fully conserved, i.e., the reactions may be written

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

Thus, since the polarization of the product electrons is equal to that of the $2\,^3S$ atoms, P_z is given directly by the measured Penning-electron polarization [8]. The $2\,^3S$ polarization was typically ~ 0.7 and would remain constant for periods of many hours.

A significant extracted-electron signal was observed in the absence of target gas that comprised electrons ejected from surfaces in the vicinity of the extraction aperture by metastable atom impact. These electrons have a broad distribution of energies [9] and their polarization is quite large, typically $\sim 70\%$ that of the $2\,^3S$ atoms. This spurious electron signal, however, is substantially reduced upon admission of target gas because the majority of the $2\,^3S$ atoms are deexcited in gas-phase collisions. Thus contributions from surface ejection are unimportant except in energy regions where the Penning-electron signal is small.

Electron-energy distributions measured following PI reactions with CO_2, CO, Cl_2, and O_2 are shown in Figs. 2(a)–2(d), respectively, together with the corresponding energy-resolved electron polarizations. (The electron polarizations are expressed as a percentage of the initial $2\,^3S$ polarization.) Figure 2 also includes EED's measured (with higher energy resolution) by earlier workers using beam and gas cell techniques [10–13]. The general features of these earlier data are reproduced well in the present work, demonstrating that electrons can be extracted from the afterglow without a significant change in energy, although the relative extraction efficiency appears to decrease at higher-electron energies.

The EED observed for CO_2 comprises a number of narrow features pointing to ionization via the covalent channel. The different features correspond to population of the ground $X\,^2\Pi_g$ and excited $A\,^2\Pi_u$, $B\,^2\Sigma_u^+$, and $C\,^2\Sigma_g^+$ states of the product $CO_2{}^+$ ion, i.e., to removal of an electron from the CO_2 $1\pi_g$, $1\pi_u$, $3\sigma_u$ and $4\sigma_g$ orbitals, respectively [10]. The electron polarization associated with the $X\,^2\Pi_g$, $A\,^2\Pi_u$, and $B\,^2\Sigma_u^+$ features is large and, to within experimental error, is equal to that of the $2\,^3S$ atoms, indicating that spin is conserved irrespective of the collision geometry (ionization into Σ states is most favorable for collinear end-on collisions, whereas side-on collisions are more effective for ionization into Π states)

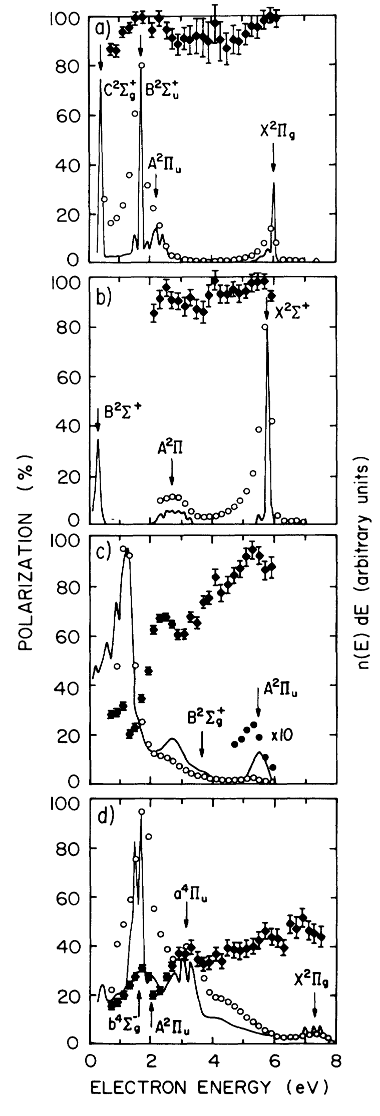

FIG. 2. Electron-energy distributions and polarization profiles measured following PI reaction with (a) CO_2, (b) CO, (c) Cl_2 and (d) O_2. ♦, electron polarizations; ○, measured energy distributions; ——, energy distributions obtained by earlier workers using beam and gas cell techniques.

[10] and the target orbital from which the electron is ejected. (The somewhat-lower polarizations observed in regions between the Penning peaks result because, in these regions, the extracted current is very small and contributions from surface-electron ejection become significant.) PI reactions with CO_2 must therefore proceed by an Auger-type process in which an electron of appropriate spin from the target molecule tunnels into the $1s_\downarrow$ hole in the $2\,^3S$ atom with simultaneous ejection of the $2s_\uparrow$ electron.

The EED associated with the PI of CO again comprises a series of relatively sharp features, which correspond to ionization into $X\,^2\Sigma^+$, $A\,^2\Pi$, and $B\,^2\Sigma^+$ states of the CO^+ ion, suggesting ionization via the covalent channel [11]. The polarization of the $X\,^2\Sigma^+$ feature is equal to that of the $2\,^3S$ atoms. The polarization of the (smaller) $A\,^2\Pi$ feature appears to be a slightly lower but this may be attributed to contributions to the extracted electron signal from surface ejection. The data thus suggest that spin is conserved in PI reactions with CO and that, as for CO_2, ionization occurs via an Auger-type process.

The EED's and polarization profiles measured with Cl_2 and O_2 are quite unlike those observed for CO and CO_2, pointing to differences in the reaction mechanisms. The EED for Cl_2 has been analyzed in detail by earlier workers [12]. The relatively sharp feature at ~ 5.4 eV results from ionization via the covalent channel into the ${Cl_2}^+$ $A\,^2\Pi_u$ state. (Smaller features at ~ 8.2 and 3.7 eV associated with ionization into ${Cl_2}^+$ $X\,^2\Pi_g$ and $B\,^2\Sigma_g^+$ states, respectively, have also been reported but were not resolved in the present work.) The broad low-energy maximum is associated with ionization via the ionic channel. (Transitions to the ionic channel are, however, symmetry forbidden if the $2\,^3S$ atom is incident in the bisector plane of the Cl_2 target [12].) The general characteristics of the low-energy portion of the EED, including the feature at ~ 2.7 eV, can be reproduced by modeling both the particle trajectories in the collision complex and the partial widths for autoionization of the complex into final $He + {Cl_2}^+ + e^-$ states. The collision complex, however, can also decay through formation of Cl_2^{**} molecular Rydberg states that dissociate into ground-state and excited Cl atoms, including core-excited atomic states of the form $Cl^{**}[3p^4(^1D)nl]$, which, if the energy of core excitation (1.45 eV) is greater than the binding energy of the *nl* electron, can undergo autoionization. The peak in the EED immediately below ~ 1.45 eV is attributed to such autoionization [12].

The polarization of those electrons that comprise the $A\,^2\Pi_u$ peak is, allowing for possible small contributions from surface ejection, equal to that of the $2\,^3S$ atoms, showing that ionization out of the covalent channel again occurs via an Auger-type mechanism. However, at the lower energies characteristic of ionization via the ionic channel, the electron polarization decreases, presumably as a result of spin-orbit (s.o.) coupling. Reactions via the ionic channel can be pictured as initially proceeding through transfer of the He $2s_\uparrow$ electron to produce a $He^+ + {Cl_2}^-$ ion pair. Electron attachment to Cl_2 results in ${Cl_2}^-$ ions in the $^2\Sigma_u^+$ state, suggesting that the polarization of a "captured" 2*s* electron will not be degraded by s.o. interactions before it is ejected from the collision complex through autoionization. Trajectory calculations, however, indicate that autoionization of a collision complex typically occurs at very small helium-chlorine internuclear separations [12]. Thus, during much of the interaction, the ${Cl_2}^-$ ion will be strongly perturbed by the He^+ ion, and it is therefore not possible to infer the behavior of the collision complex simply from that of isolated ${Cl_2}^-$ ions. The existence of strong internal interactions could induce an orbital electronic moment and hence s.o. coupling, which could cause a reduction in electron polarization because the axis about which spin precession occurs will depend on the geometrical arrangement of the nuclei and will change during the collision. The decrease in polarization observed with decreasing electron energy may then be qualitatively explained by noting that lower electron energies correlate with ionization at smaller internuclear separations which would (presumably) allow stronger s.o. coupling and a greater change in nuclear positions.

The pronounced polarization minimum at ~ 1.5 eV is associated with contributions to the electron signal from autoionization of excited $Cl^{**}[3p^4(^1D)nl]$ atoms. Such autoionization produces Cl^+ ions in ^3P states and must therefore occur via an exchange process in which the *nl* electron is captured in the core ejecting a 3*p* electron. Thus, a reduction in the electron polarization is expected (the 3*p* electrons are unpolarized). Indeed, the observation of a pronounced polarization minimum confirms the importance of Cl^{**} autoionizing states. No simple explanation for the polarization minimum at ~ 2.8 eV, which correlates with a local maximum in the EED, has yet been found.

The EED for O_2 comprises a broad, relatively featureless background associated with ionization via ionic channels, superimposed upon which are a number of sharp peaks corresponding to ionization from the covalent entrance channel into the $X\,^2\Pi_g$, $a\,^4\Pi_u$, and $b\,^4\Sigma_g^-$ states of the ${O_2}^+$ ion [13]. The measured electron polarizations are much smaller than for the other targets studied in this work, and even the $X\,^2\Pi_g$ covalent channel does not result in a large electron polarization. This is not unexpected, because (unlike CO_2, CO, and Cl_2) O_2 is an open-shell molecule, and the polarization of the incoming $2\,^3S$ atom can be degraded prior to ionization by exchange between the He 2*s* and O_2 $1\pi_g$ electrons. The low polarization associated with ionization via ionic channels can be explained by considering the possible spin states for the reactants, which are

$$He(2\,^3S)\{\uparrow\uparrow\} + O_2[\cdots 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2]\begin{cases}\{\uparrow\uparrow\} & \text{(3a)}\\ \{\uparrow\downarrow\} & \text{(3b)}\\ \{\downarrow\downarrow\}\ . & \text{(3c)}\end{cases}$$

The reacting system can form quintet, triplet, and singlet spin states, but the ionic channel is only accessible for the latter two (${O_2}^-$ and He^+ each being spin doublets). The three $|M_S(\mathrm{He}), M_S(\mathrm{O_2})\rangle$ entrance channels can be expressed in terms of the possible $|S,M_S\rangle$ states for the total system as $|1,1\rangle = |2,2\rangle$; $|1,0\rangle = (1/\sqrt{2})\{|2,1\rangle$

$+|1,1\rangle\}$; $|1,-1\rangle=(1/\sqrt{6})|2,0\rangle+(1/\sqrt{2})|1,0\rangle+(1,\sqrt{3})|0,0\rangle$. Thus, since reaction from the quintet entrance channel is spin forbidden, reaction will not occur for case (3a); for case (3b), reaction will proceed, on average, in only $\frac{1}{2}$ of the collisions, while for case (3c), reaction is possible in $\frac{5}{6}$ of the collisions. Energy conservation requires that the portion of the EED above 4 eV correspond to ionization into the O_2^+ $X\,^2\Pi_g$ ground state, whereupon, assuming that the probability that an electron be ejected from the O_2^- $1\pi_g$ orbital is independent of its spin, case (3b) [(3c)] will result in electrons with 100% (0%) polarization. Thus if cases (3b) and (3c) are equally likely, the net polarization of the ejected electrons will be 37.5% (independent of any earlier exchange between He 2s and O_2 $1\pi_g$ electrons), in good agreement with the experimental observations. The decrease in polarization at energies approaching 4 eV might again be attributed to s.o. interactions. At lower energies, contributions to the total electron signal from ionization into excited O_2^+ states must be considered. In such reactions, the electron that tunnels into the He $1s_\downarrow$ core hole must originate from the O_2^- $1\pi_u$ or $3\sigma_g$ orbital and the ejected electron from the $1\pi_g$ orbital, or vice versa. Consideration of the electron polarizations associated with cases (3b) and (3c) then suggests a net polarization close to zero. Thus, the polarization profile below 4 eV may be qualitatively explained by attributing the relative maxima at $\sim$1.7 and 3.2 eV to ionization into O_2^+ $b\,^4\Sigma_g^-$ and $a\,^4\Pi_u$ final states via the covalent channel, with underlying contributions from ionic channel ionization into both ground and excited O_2^+ states.

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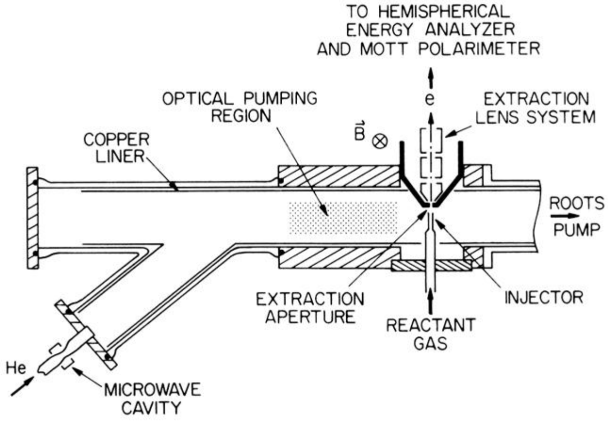

FIG. 1. Schematic diagram of the apparatus.