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Spin conservation during chemi-ionization and surface-electron ejection by He(2 ^3S)†

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The conservation of spin angular momentum during inelastic collisions of spin-oriented metastable He(2 ^3S) atoms with contaminated surfaces and a variety of gaseous targets, including Ar, H_2, N_2, CO, CO_2, and N_2O, has been investigated. The metastables are contained in a flowing helium afterglow and are oriented by optical pumping. The electrons produced during subsequent chemi-ionization and surface-ejection reactions are extracted and spin analyzed by Mott scattering. Spin angular momentum is found to be fully conserved for all the reactions studied, with the possible exception of the chemi-ionization of CO. The experimental results are discussed in the light of existing theories and models for chemi-ionization. The results also suggest that secondary electron ejection from chemically cleaned surfaces occurs through chemi-ionization of adsorbed species.

I. INTRODUCTION

In recent years there has been considerable interest, both theoretical and experimental, in collision processes involving metastable helium atoms in the 2 ^3S state. The internal energy of 19.8 eV associated with this state is sufficient to allow a broad spectrum of chemi-ionization reactions of the types

$$\begin{aligned}\mathrm{He}(2\,^3\mathrm{S}) + AB &\rightarrow \mathrm{He}(1\,^1\mathrm{S}_0) + AB^+ + e^-\\ &\rightarrow \mathrm{He}(1\,^1\mathrm{S}_0) + A + B^+ + e^-\\ &\rightarrow \mathrm{He}AB^+ + e^- \qquad (1)\\ &\rightarrow \mathrm{He}A^+ + B + e^-\\ &\rightarrow \mathrm{He}(1\,^1S_0) + A^+ + B^-\end{aligned}$$

to occur during collisions with gaseous targets, with the exception of neon. He(2 ^{3}S) atoms are also capable of efficient secondary-electron ejection from metal surfaces, even when incident at thermal energies.

Despite extensive studies of both chemi-ionization and secondary-electron ejection it is only recently that a detailed understanding of such reactions has begun to emerge.[1-3] In the present work an optical-pumping technique[4] is employed to spin orient the He(2 ^{3}S) atoms present in a flowing helium afterglow. The degree to which this electron-spin orientation is transferred to the electrons produced during subsequent chemi-ionization and surface reactions is then determined, thereby providing information about the dynamics of both electron-production processes. In both cases spin angular momentum is found to be generally well conserved and the implications of these findings are discussed. The conservation of spin angular momentum during chemi-ionization collisions has been utilized to develop an intense source of polarized electrons, which is described in the following paper.[5]

II. EXPERIMENTAL APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. Briefly, the apparatus comprises an optically pumped, low-pressure (~0.1 Torr) flowing helium afterglow, an extraction system to enable the electrons produced either in the afterglow or by secondary-electron ejection resulting from metastable impact with the extractor to be sampled, and a Mott analysis system to determine the spin polarization of the extracted electrons.

The afterglow is contained in a 10-cm-diam Pyrex tube exhausted by a 500 1-sec^{-1} Roots pump. The velocity distribution across the tube is nearly parabolic (as expected for viscous flow) with an average, or bulk flow, velocity of 4.2×10^3 cm sec^{-1}. Metastable excitation is accomplished using either a microwave discharge[6] or a movable electron gun, the high-purity helium being introduced through the appropriate arm of the "*Y*" shown in Fig. 1.

Both He(2 ^{3}S) and He(2 ^{1}S) metastables are produced by these sources. The 2 ^{1}S to 2 ^{3}S ratio decreases from 0.07 to 0.02 and 0.5 to 0.2 for the microwave and electron-gun sources, respectively, as the afterglow pressure is increased through the operating range of 0.08–0.15 Torr. The electron density in the flow tube when no reactant gas is added is so low that the 2 ^{1}S metastables are not converted to the 2 ^{3}S state by electron exchange as is common in higher-pressure afterglows. Thus the He(2 ^{1}S) atoms contribute to any electron-production process present in the afterglow and these electrons are necessarily unpolarized. However the singlet contribution to the extracted electron currents may be determined because the

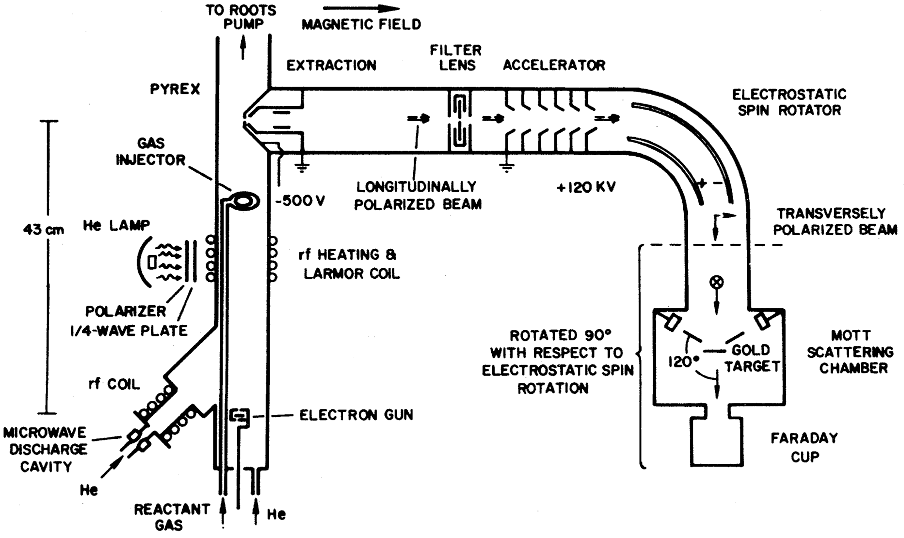

FIG. 1. Schematic diagram of the experimental apparatus (not drawn to scale).

ratio of the $2\,^1S$ and $2\,^3S$ populations is monitored by optical-absorption measurements thereby permitting the electron polarizations resulting from $2\,^3S$ interactions to be uniquely determined. This correction is, however, very small when using the microwave cavity and as a result this source was used to obtain the majority of the data reported in this paper. The cavity was placed off axis to prevent the direct illumination of the optical-pumping and extraction regions with 1.08-μm ($2\,^3S - 2\,^3P$) photons emitted from the microwave cavity. Molecular ions and metastables, which are formed primarily by three-body reactions[7,8]

$$\begin{aligned} He^+ + 2He &\rightarrow He_2^+ + He, \\ He^* + 2He &\rightarrow He_2^* + He, \end{aligned} \tag{2}$$

are not significant at the low pressures used in the experiment.

Chemi-ionization reactions are studied by injecting a reactant gas into the helium flow stream through a movable perforated ring. A manifold is provided on the gas inlet system to enable two or three gases to be admitted in rapid succession, thereby enabling normalization of each data set. The reaction length employed, defined as the distance from the gas injector to the extraction aperture, is typically 4–15 cm. The optical-pumping lamp and microwave cavity were located 25 cm and 50 cm, respectively, upstream of the extraction aperture.

A. Optical pumping

The He($2\,^3S$) atoms are optically pumped to the $m_s = +1$ (or -1) state in the usual manner[4] by right (or left) circularly polarized 1.08-μm resonance radiation from an intense helium discharge lamp. The absorption of 1.08-μm ($2\,^3S - 2\,^3P$) and 2.06-μm ($2\,^1S - 2\,^1P$) radiation, from which the density of the $2\,^3S$ and $2\,^1S$ atoms can be determined,[9] is measured using narrow-band interference filters and a PbS photodetector. Helmholtz coils of 6-ft diameter, provide a uniform magnetic field of 5 G over the entire flowing-afterglow region, thus defining a unique quantization axis parallel to the pumping light.

The optical pumping does not, however, align all the $2\,^3S$ atoms in the $m_s = +1$ state because of competitive thermalization processes. The relative populations of the $m_s = +1$, 0, and -1 sublevels—and hence the induced metastable polarization P_m, defined for purposes of this work as

$$P_m = (N_+ - N_-)/(N_+ + N_0 + N_-), \tag{3}$$

where N_+, N_0, and N_- are the populations of the $m_s = +1$, 0, and -1 states, respectively—can in principle be determined by measuring the change in fractional absorption of the pumping radiation when the $2\,^3S$ polarization is destroyed by application of an rf magnetic field at the magnetic resonance frequency. Details of this method are discussed elsewhere.[4,10] The reliability of the method is severely limited by its high sensitivity to both the spectral positions and profiles of the pumping radiation (from an rf-excited helium lamp) relative to those of the absorber, and to the experimentally unavoidable small deviations from the thin-absorber limit. As a result the $2\,^3S$ polarization, P_m, determined in this manner must be regarded as semiquantitative, and is estimated to lie between 25% and 35%. This polarization is in accord with that deduced by Schearer using a similar flowing-afterglow apparatus.[11]

"Depumping" transitions result from radiation trapping of the $2\,^3P$-$2\,^3S$ pumping light. The optically induced spin polarization is therefore somewhat dependent on the $2\,^3S$ density and is decreased by ~20% as the fractional absorption of the pumping light increases from 1.3% to 12% (corresponding to an increase in $2\,^3S$ density from about 10^9 to 10^{10} cm^{-3}). Thus the $2\,^3S$ density was maintained at a low value (~10^9 cm^{-3}) while taking the present data.

B. Electron extraction and spin analysis

The electrons are extracted through a small, interchangeable aperture located at the end of a truncated cone protruding into the afterglow as shown in Fig. 1. Several aperture geometries were tested, ranging from a canal of 1.5-mm diameter by 1.5-mm length to an orifice 2-mm diameter by 0.2-mm length. The aperture size and the flow-tube pressure are limited by the pumping speed available to evacuate the beam tube into which the electrons are extracted.

The extracted electron-beam energy of 500 eV is achieved by biasing the entire flow tube and extraction aperture negative with respect to the extraction anode, located immediately behind the extraction aperture. An Einzel lens focuses the beam onto the entrance aperture of a filter lens which can be used for measuring the electron energy distribution. For polarization measurements the filter lens was operated as a simple Einzel lens with a center aperture of 1-in. diameter. Measurements of the energy distribution of the beam are discussed in the following paper. Beam current is monitored by inserting a movable collector into the beam near the extractor.

The polarization of the electron beam is determined using Mott scattering.[12] Details of the technique used in these experiments have been described by McCusker.[10] The electron beam, which is extracted with longitudinal spin polarization, is first accelerated to 120 keV. The velocity vector is then rotated 90° with respect to the spin vector to obtain a transversely polarized beam.[13] The spin polarization P_e, defined as

$$P_e = (n_+ - n_-)/(n_+ + n_-) \tag{4}$$

where n_+ and n_- are the populations of the $m_s = \pm\frac{1}{2}$ states, respectively, is determined from the small azimuthal asymmetry produced by spin-orbit coupling in the elastic scattering of the electrons from a thin gold foil at a scattering angle of $\theta = 120°$. If the sense of the circularly polarized 1.08-μm optical-pumping radiation is reversed, then so too is the direction of the electron polarization. Systematic instrumental asymmetries may therefore be readily eliminated and the true electron polarization determined by measuring the scattering asymmetry from the gold foil for both electron beam polarizations, as is discussed elsewhere.[10]

C. Origins of extracted current

In order to correctly interpret the data it is necessary to understand and isolate the origins of the extracted electron currents.

In the afterglow, the rate of electron loss is proportional to the ambipolar diffusion coefficient D_a, which is related to the free-ion diffusion coefficient D_+ by the relation $D_a = D_+(1 + T_e/T_+)$, where T_e and T_+ are the electron and ion "temperatures." For $T_e = T_+ = 300$°K, the value of D_a for He$^+$ ions in He measured by Oskam and Mittelstadt[14] is nearly equal to the diffusion coefficient for triplet metastables measured by Phelps.[8] However, the electron temperatures in at least the first few centimeters from the metastable source are considerably above 300°K. Therefore it is expected that, at the low pressures of these experiments, where the diffusion time is of the same order or less than the thermalization time, the ratio of electrons to metastables will be very small at the position of the extractor, typically 50 cm from the source. This expectation is confirmed by the observation that, when no reactant gas is injected, the extracted current is not significantly decreased when diffusion of electrons to the walls of the flow tube is enhanced through rf heating by means of an external coil.

Thus in the absence of any reactant gas, the extracted current I_s (for $I_s \gtrsim 10^{-10}$ A) is attributed to electron ejection resulting from metastables hitting the walls of the extraction aperture. The current magnitudes are approximately as expected from the metastable diffusion rates to the aperture, and the current is linear with respect to metastable density as may be seen from Figs. 2(a) and 2(b). The observations rule out any significant electron production by ionizing collisions between two metastables, a nonlinear process and one whose rate is far too low to account for the measured currents.[15] Any electron production by metastable ionization of impurities in the flow tube also falls far short of accounting for the measured currents.

If reactant gas is introduced into the afterglow, a somewhat reduced current of electrons I_c is extracted. In practice sufficient reactant gas is added to reduce typically the metastable density by a factor of 100 4 cm downstream from the injector. Thus essentially no metastables strike the extractor aperture, and the extracted electron current must consist of electrons produced during chemi-ionization collisions. The slight reduction

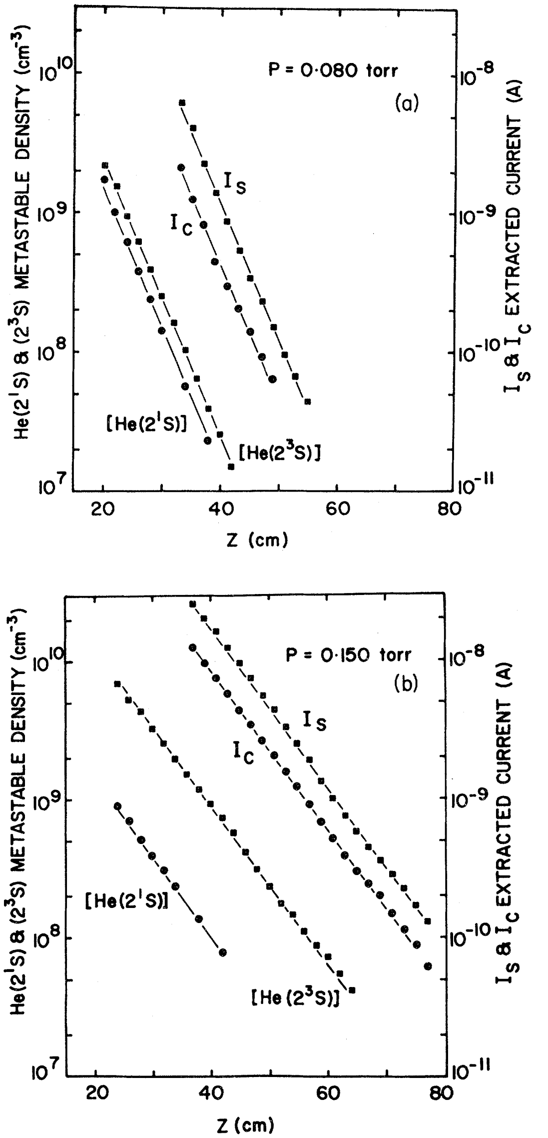

FIG. 2. Average He($2\,^3S$) and He($2\,^1S$) metastable densities in the flow tube, and extracted currents I_c and I_s as a function of separation z of the extractor and electron-gun metastable source. Metastable densities are measured 13 cm upstream of the extractor. I_c is the electron current resulting from chemi-ionization of argon 4 cm upstream of the extractor, and I_s that resulting from secondary-electron ejection by metastables striking the brass extractor surface when no reactant gas is introduced. The data in (a) and (b) are for helium pressures of 0.08 Torr and 0.15 Torr, respectively, in the flow tube.

in extracted current presumably results because the fast electrons produced during chemi-ionization are lost more rapidly by diffusion than are the metastables as the gas flows from the reaction region to the extractor. As expected I_c is proportional to the metastable density, as shown in Figs. 2(a) and 2(b), and can be reduced by two orders of magnitude by rf heating of the reaction region.

Secondary-electron ejection at the extractor by the chemi-ions could result in an extraneous contribution to I_c. However, the available data indicate that the secondary-electron yields for argon[16] and a variety of molecular ions[17,18] are quite small, and conservative estimates of the contribution to I_c from this source show it to be certainly less than 10% and probably less than 5%.

Ionization of the background gas in the post-extraction region by the extracted electron beam provides a further extraneous source of electron production. Such a contribution to the measured current is easily eliminated by reducing the gas load on the post-extraction vacuum system by use of a small extraction aperture (1.5-mm diameter, 1.5-mm length) and afterglow pressures well below 0.15 Torr.

It is thus possible to operate the apparatus in regions in which the origins of the extracted electron currents are well understood.

III. RESULTS AND DISCUSSION

A. Chemi-ionization

Electron polarizations were measured for the chemi-ionization of Ar, H_2, N_2, N_2O, CO, and CO_2 by spin-polarized He($2\,^3S$) metastables over a range of flow-tube pressures from 0.08 to 0.17 Torr. The measured values of P_e (as corrected for the $2\,^1S$ contribution) are presented in Table I. The measured polarizations P_e and the quoted errors represent in each case the mean value and day-to-day variations of a large number of polarization measurements from several data sets obtained over a period of several weeks.

As expected, the measured electron polarizations were found to be insensitive to afterglow pressure over the range 0.10–0.15 Torr, to aperture geometry and extraction potential, and to the excitation source used (microwave or electron gun), provided that corrections are made for contributions to the extracted currents arising from $2\,^1S$ interactions.

With the exceptions noted below, it was also verified experimentally that the results are insensitive to injector-extractor separation for the reactant gases studied—all of which have spin-singlet ground states. This demonstrates that the results are not influenced by spin-changing collisions with ions or neutral reactant gas downstream of the chemi-ionization reaction region. However, marked polarization degradation *was* noted when nonsinglet reactant gases such as $O_2(^3\Sigma_g^-)$ and $NO(^2\Pi_g)$ were injected, presumably as a result of spin-exchange reactions along the reaction length prior to extraction. This effect precluded the study of these gases in the present experiment, but does suggest the possibility of measuring spin-exchange reaction rates in a suitably modified apparatus.[19]

With the exception of CO, which will be discussed later, all the measured chemi-ionization electron polarizations P_e lie between 27% and 31%, with experimental errors estimated to be less than $\pm 0.1\ P_e$. These values agree with the estimated He$(2\,^3S)$ polarization P_m produced by optical pumping, thereby suggesting that spin angular momentum is conserved during chemi-ionization reactions. However, a more compelling argument for complete spin conservation is the fact that the electron polarizations from all reactions are approximately the same. It would indeed be surprising if all gases exhibit the same fractional polarization transfer.

Conservation of spin angular momentum in the reaction

$$\mathrm{He}(2\,^3S) + \mathrm{He}(2\,^3S) \rightarrow \mathrm{He}^+ + \mathrm{He}(1\,^1S) + e \qquad (5)$$

has been demonstrated qualitatively by Schearer and Riseberg,[20] and by McCusker, Hatfield, and Walters[10] while Hill *et al.*[21] have shown quantitatively that it is fully conserved. Schearer has further demonstrated the conservation of both the direction and phase of electron spin in chemi-ionization reactions of oriented He$(2\,^3S)$ atoms with group-II metals,[22,23] by monitoring the optical polarization of the light emitted by product ions which are formed in excited states, or that absorbed by ground-state product ions.[24] This method is limited however, in that spin polarization must be transferred via spin-orbit coupling to align the orbital moment which is detected in the measurement. Therefore quantitative determination of the degree of spin angular momentum conservation is difficult, especially when the technique is extended to molecules where both spin-orbit and spin-rotational coupling can rapidly degrade the induced polarization. The N_2 molecule is an example of a system subject to this difficulty. The polarization of light emitted by the $N_2^+(B\,^2\Sigma_u)$ state is less than 2% of that emitted by cadmium ions,[25] whereas the results of the present experiment show that spin orientation is completely conserved in the chemi-ionization of N_2.

A number of theoretical approaches to chemi-ionization reactions have been proposed, invoking as models orbiting collisions, excitation transfer, and autoionization.[1-3] The latter has proven to be the most successful for calculating the cross section and electron energy distribution for the He$(2\,^3S)$+H system.[26] The observation that spin angular momentum is conserved during chemi-ionization collisions is consistent with only the two-state potential model for chemi-ionization that is often discussed.[1-3] According to this model, the entrance channel is described by a potential $V(R;\ \mathrm{He}^*, AB)$ that is a function of the separation R of the metastable helium atom from a molecule AB. This potential curve is embedded in the continuum of several possible exit channels described by potentials such as $V(R;\ \mathrm{He}, AB^+)$ in the case of Penning ionization. The chemi-ionization event is described as a vertical or Franck-Condon autoionizing transition from the entrance to the exit channel. The correctness of this model has been demonstrated for chemi-ionization of a number of atoms and molecules (including H_2, N_2, and CO from among those studied here) by measurements of the product electron energy distributions,[27] and of the relative vibrational level populations of the product ions.[28-30]

Chemi-ionization reactions for which this model holds must always conserve spin angular momentum, since the vertical transition effectively precludes the possibility of formation of intermediate molecular reaction complexes with sufficiently long lifetimes ($\gtrsim 10^{-12}$ sec) for magnetic interactions to perturb the electron spin states. Thus the experimental results presented here provide further confirmation of the Hotop-Niehaus[31] model for the atoms and molecules studied.

The present results strongly suggest that for the target gases studied chemi-ionization does not proceed through the formation of a relatively long-lived intermediate state prior to the escape of the free electron, when spin-orbit or spin-rotational coupling could seriously degrade any initial electron-spin polarization.

TABLE I. Measured values of polarizations P_e of electrons produced in chemi-ionization reactions He$(2\,^3S) + AB \rightarrow e^-$ + other products [Eq. (1)], and for electrons ejected from the brass extractor surface upon He$(2\,^3S)$ impact. The He$(2\,^3S)$ polarization was approximately 30%. The P_e values reported have been corrected for a small (~5%) $2\,^1S$ contribution to the extracted currents. The experimental errors are estimated to be less than $\pm 0.1 P_e$.

AB	P_e
Ar	0.28
H_2	0.29
N_2	0.31
CO	0.22
CO_2	0.30
N_2O	0.27
Brass surface	0.27

A particularly interesting extension of the present experiment is suggested by the recent observation that the vibrational populations of the $A\,^2\Sigma^+$ states of HCl^+ and HBr^+ formed in Penning-ionization reactions with He($2\,^3S$) metastables are *not* in accord with a vertical process.[30] Thus, spin-conservation measurements on these systems may provide information on the nature and lifetimes of any intermediate complexes formed.

Of the reactions studied in the present work, chemi-ionization of CO is the only one for which the product electron polarization is significantly lower than expected. Since the difference is only about two standard deviations, it is difficult to conclude with certainty that spin angular momentum is not fully conserved; however it is interesting to note that there is a near resonance between He($2\,^3S$) and the lowest $CO^+(B\,^2\Sigma^+)$ vibrational states ($v=0$ at 19.67 eV and $v=1$ at 19.88 eV) as pointed out by Richardson and Setser.[30] This suggests the possibility of the formation of a long-lived intermediate (CO-He)* complex which may subsequently autoionize or dissociate to produce C^*+O. Excited carbon atoms are observed in 4% of the He($2\,^3S$)+CO reactions.[32] The estimated relative population of the $CO^+(B)$ state is sufficient to account for a significant reduction in spin polarization observed if this level is indeed produced via a long-lived collision complex. It is difficult to say whether or not the measured vibrational populations of the $CO^+(B)$ state, ($v_0:v_1=100:17$),[30] are in accord with the Franck-Condon factors ($v_0:v_1:v_2=100:40:15$) because the populations are limited primarily by the available energy. [The $v=1$ state is 0.061 eV above the He($2\,^3S$) state.] Further study of this reaction using polarization analyses of the radiation from the $CO^+(A)$ and $CO^+(B)$ states may clarify the role of excitation transfer.[11]

The N_2O and CO_2 chemi-ionization reactions are also particularly interesting because spin angular momentum conservation alone does not require that the product electrons fully preserve the spin orientation of the He($2\,^3S$) metastable atom. West[33] has recently measured the relative probabilities of the various chemi-ionization reactions possible during the collision of He($2\,^3S$) with N_2O and CO_2. The results are,

for N_2O, 50.5% ($NO^+ + N$); 47.1% (N_2O^+);
2.4% ($O^+ + N_2$);
for CO_2, 68.5% (CO_2^+); 26.7% ($O^+ + CO$);
4.8% ($CO^+ + O$).

In the case of CO_2, the available energy requires the dissociated products to be produced in their ground states, in particular $O(^3P)$ and $O^+(^4S)$, both of which have the capacity to absorb all the angular momentum in the entrance channel. The fact that the He($2\,^3S$) spin angular momentum is observed to be fully transferred to the product electrons, while 30% of the CO_2 reactions would not require it, supports the suggestion of Hotop and Niehaus[31,34] that chemi-ionization proceeds via an electron-exchange process. A similar argument can be made for the N_2O reaction, although in this case energy conservation does not require the dissociated products to be produced in their ground electronic states.

Finally, it is perhaps worthy of note that upper limits on cross sections for electron exchange with ions produced in the chemi-ionization region can be derived from the observation that within the limits of experimental error there is no electron polarization degradation (with the exception of N_2O) as the injector-extractor separation is increased, thereby increasing the interaction time prior to the extraction. The upper limit in all cases is about 3×10^{-14} cm^2, while for N_2O (for which a slight polarization degradation is observed) it is 8×10^{-14} cm^2. The polarization degradation from N_2O can alternatively be attributed to electron exchange with product $N(^4S)$ atoms to yield an upper limit of 4×10^{-14} cm^2 for that cross section. Refinements in the experimental technique should make it possible to measure these cross sections or to establish much more stringent upper limits.

B. Surface interactions

The polarization of surface-ejected electrons emitted as a result of collisions of the He($2\,^3S$) atoms with the brass extraction aperture is included in Table I and is seen to lie in the same band of polarizations observed from chemi-ionization of the atoms and molecules studied, thereby strongly suggesting that spin is conserved in electron-ejecting He($2\,^3S$) surface reactions. This result is at variance with accepted theoretical models for electron ejection from atomically clean metallic surfaces, in which the ejected electron is thought to come from the conduction band of the metal and has therefore no spin-orientation preference.[16] The surface of the extractor is however not atomically clean and the observed high degree of spin angular momentum conservation suggests that ejection occurs through the chemi-ionization of loosely bound absorbed species, in partial agreement with the work of Allison *et al.*[35] and Donnally *et al.*[36]

Allison *et al.* measured the energy spectrum of electrons ejected from a contaminated stainless-steel surface and observed a double-peaked distribution. They suggest that the higher-energy electrons (4–13 eV) are produced by chemi-ionization of adsorbed species. However, since the high-energy peak accounted for only $\frac{1}{3}$ of the total yield of electrons, total spin conservation is not to be expected. Donnally *et al.*[36] have reported a spin-polarization transfer of 66% from an oriented He($2\,^3S$) atomic beam to electrons ejected from contaminated gold and tungsten surfaces.

Allowing for the experimental uncertainty in the measurements reported here, we conclude that for the present contaminated brass extractor surface essentially all of the surface-ejected electrons preserve the spin orientation of the incident He($2\,^3S$) atoms and probably result from chemi-ionization of adsorbed atoms. Thus there seems to be qualitative agreement between all three experiments that many electrons ejected from contaminated surfaces do result from chemi-ionization. However the results of the present experiment suggest that a much lower fraction of electrons come from the metal itself than would be expected from the energy distribution measured by Allison *et al.*, or the results of Donnally *et al.*, perhaps reflecting only that the surfaces employed in the three experiments are different.

It would be interesting to extend these polarization transfer measurements to include polarized He($2\,^3S$) and He$^+$ ions incident on atomically clean surfaces. This would further test the assumed identity of the ejection process for these two species, and test for any spin correlation between the two electrons involved in the Auger neutralization of an incident ion.

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