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RICE UNIVERSITY

SINGLE-MODE FREQUENCY-STABILIZED
1.083 µM RING LASERS

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

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Single-Mode, Frequency-Stabilized 1.083 μm Ring Lasers

by

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Abstract

A single-mode, frequency-stabilized LNA ring laser has been developed which routinely provides output powers ≥ 300 mW at 1.083 μm when pumped with 5 W of the 514 nm output from an Argon ion laser. A modified CR899-21 Ti:Sapphire ring laser from Coherent Laser Group of Palo Alto produces 300 mW at 1.083 μm when pumped with 21 W of all-lines Argon ion laser light.

The importance of intense, stable 1.083 μm laser sources is demonstrated through several experiments. Optical pumping with either laser produces He(2^3S) atom beams of high polarization which can be maintained for periods of many hours. This allows investigation of Penning Ionization using spin labeling techniques, spin-polarized metastable atom deexcitation spectroscopy, and a novel method for absolute calibration of Mott polarimeters. Saturation of the He(2^3S) → He(2^3P) transition allows study of the interaction of mixed He(2^3S)/He(2^3P) atoms beams with surfaces. Construction of a magneto-optical trap for He(2^3S) atoms is possible utilizing the high power provided by the laser systems.

Both lasers provide ample power for all applications currently envisioned involving optical pumping and optical manipulation of He(2^3S) metastable atoms.
Acknowledgments

It seems like my masters was not all that long ago, and it really wasn’t. All the people who were important then, are still important now. I suppose, then, this is my big opportunity to thank all the people I missed the first time around; I assure you, it was not intentional. In my rush to get this thesis completed, and the tension of a job search in this post-Bush era, some people will again be forgotten. For this I am deeply sorry.

To Vicki (and the guys), Belldandy, P-Chan, scary eyes, peaches, cher, little sneezer, Vicki Lynn: some things you know you will live to regret, but time and tide leave you with very little choice. If I were more certain about my own future, I could be more certain about ours. You have been, and always will be, very special to me.

I have always lived like a nerd, but missed many of the advantages of being a nerd. For filling in the gaps in my nerd-training, I have Greg Morrow, a nerd who really knows how to live, to thank. Houston would have been at least 2.63 times more dull without you.

I would like to thank my family for their unswerving support, but I can’t because it swerved a few times. I guess I’ll thank them then for keeping it between the traffic cones, or at least for never allowing their support to end up in a ditch or scratch up its paint really badly. No family is perfect, but I think we do pretty damn well, don’t you?

And I must once again thank my fellow grad studs past and present. The days you think you just can’t take it anymore, there’s always a deep philosophical discussion going on to take you away from it all (by the way, crunchy is better). We learn from and support each other. I think I have only one more important thing to teach you all:

"While you are going about your other duties, be sure to look for the flashing light and listen for the beeping alarm. These will warn you that the fries are done."

-McDonald’s training manual

I certainly couldn’t have done it alone. This round’s on me.
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Chapter One
Introduction

Many experiments with He(2\textsuperscript{3}S) metastable atoms involve the use of 1.083 \textmu m radiation to excite $2\textsuperscript{3}\text{S}_1 \leftrightarrow 2\textsuperscript{3}\text{P}_{0,1,2}$ transitions. For example, optical pumping on the $2\textsuperscript{3}\text{S} \leftrightarrow 2\textsuperscript{3}\text{P}$ transitions forms the basis of spin labeling techniques used to probe He(2\textsuperscript{3}S) reaction dynamics (see, for example, D. M. Oro et al., 1992c; D. M. Oro et al., 1994a) and of the flowing Helium afterglow polarized electron source (see, for example, G. H. Rutherford et al., 1990; S. Essabaa et al., 1991). In addition, $2\textsuperscript{3}\text{S} \leftrightarrow 2\textsuperscript{3}\text{P}$ transitions are used to optically manipulate and trap He(2\textsuperscript{3}S) atoms (see, for example, N. Vansteenkiste et al., 1991; F. Bardou et al., 1992).

Initially, the only available sources of 1.083 \textmu m radiation were high-power helium discharge lamps that provided very limited intensities. Recently, however, a number of solid-state materials have become available that can serve as the basis of lasers operating at 1.083 \textmu m. Among these materials are Nd:YAP (C. L. Bohler et al., 1988), Ti:Al\textsubscript{2}O\textsubscript{3} also known as Ti:Sapphire (see, for example, P. F. Moulton, 1986; A. Sanchez et al., 1986), Neodymium-doped Lithium Niobate (L. D. Shearer et al., 1987), and Lanthanum Neodymium Magnesium Hexaluminate (La\textsubscript{1-x}Nd\textsubscript{x}MgAl\textsubscript{11}O\textsubscript{19}, x~0.1) also known as LNA.

Due to the fact that LNA lases strongly and easily at 1.083 \textmu m, it is frequently utilized as the gain medium for lasers designed for Helium optical pumping applications. A number of different arrangements have been used in 1.083 \textmu m lasers, with the intent of achieving either higher output powers or greater stability, including (see Table 1): diode pumping of LNA (J. Hamel et al., 1987; A. Cassimi et al., 1987), LNA lasers with novel cavity designs (C. S. Adams et al., 1993), flashlamp excitation of LNA (S. Essabaa, et al., 1991), and pumping of LNA with a dye laser (P. Zhao et al., 1989). Additionally
<table>
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</tr>
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<td>J. M. Daniels et al., 1987</td>
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<td>J. Hamel et al., 1987</td>
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<td>L. D. Schearer et al., 1986</td>
<td>Ar$^+$/Kr$^+$ pumped linear LNA</td>
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</tr>
<tr>
<td>K. Kato, 1984</td>
<td>all lines Ar$^+$ pumped Styryl-14 linear dye</td>
<td>~100 mW multimode, not repeatable</td>
</tr>
<tr>
<td>K. W. Giberson et al., 1982</td>
<td>HITC dye laser (870 nm) pumped ring NaF color center laser</td>
<td>55 mW single mode with 400 mW pump</td>
</tr>
<tr>
<td>T. W. Riddle, 1981</td>
<td>400 - 600 W rf Helium discharge lamp</td>
<td>12 mW/cm$^2$ (estimated)</td>
</tr>
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</table>

Table 1: Comparison of various 1.083 μm radiation sources. All sources are CW. Argon ion pumping refers to the 514 nm line from the Ar$^+$ laser. All lines Argon ion pumping refers to the 488-514 nm output. Krypton ion pumping refers to the 752 nm output. The rf discharge lamp is included for comparison. The value quoted is calculated assuming a 50% polarization of the atom beam.
there have been several LNA lasers designed using Argon ion lasers as the pump source (see, for example, J. M. Daniels et al., 1987; L. D. Schearer et al., 1986). Although LNA does not strongly absorb the 514 nm from the ion laser, it is still a convenient pump source for several reasons. Argon ion lasers produce beams of high mode quality and good power density, with very little power fluctuation in either the short or long term. Additionally, they are available in a number of output power ranges, and give dependable, turn-key operation for hundreds of hours without significant maintenance.

A single-mode, frequency-stabilized LNA ring laser has been developed specifically as a source of tunable 1.083 µm radiation for use in He(23S) studies. This laser utilizes the temperature-controlled reference cavity, the control electronics, and many of the optical components from an earlier standing-wave LNA laser constructed in this laboratory (J.G. Lynn et al., 1990). but provides a nearly four-fold increase in the output power and efficiency. Single-frequency output powers ≥ 300 mW are routinely achieved and are significantly higher than have been reported previously with similar lasers.

Ti:Sapphire is in many ways is a more versatile lasing material than LNA due to its broad tuning range (670 - 1100 nm), although 1.083 µm lies at the edge of its gain curve. Nonetheless, with some modifications, we have been able to operate a CR899-21 ring laser from Coherent Laser Group of Palo Alto obtaining over 300 mW at 1.083 µm when pumped with 21 W of the all-lines output from an Argon ion laser.

Application of both the LNA and Ti:Sapphire lasers to studies involving helium optical pumping will be discussed.
Chapter Two
The Theory of Laser Design

A. Laser System Requirements

The design of a laser system is dependent upon the applications for which it will be used. Therefore, the requirements of the application with respect to power, stability, tunability, and linewidth must be studied. The laser system must be designed to fulfill the needs of its applications today, and, if practical, to satisfy the requirements of applications in the foreseeable future.

The lasers we have designed in the present work are used in a variety of applications involving He(2³S) metastable atoms. The transitions of interest, He(2³S)₁ → He(2³P)₀₁₂, span a wavelength range from 1083.20 nm through 1083.35 nm, so the laser should tune smoothly over that range.

Much of the research done in this laboratory incorporates transverse optical pumping of metastable atoms beams, therefore the width of the transition is governed by natural broadening, and is given by:

$$\Delta \nu = \frac{1}{2\pi \tau}$$  \hspace{1cm} (2-1)

Where \( \tau \) is the lifetime of the upper state (98.2 ns). This gives a linewidth of the transition of 1.6 MHz. The laser, then, must be stable to within just a few megahertz throughout the course of the experiment or risk drifting off the transition.

The separation between the 2³S₁ → 2³P₀, 2³P₁, 2³P₂ transition is 30 GHz and 2.3 GHz respectively. The linewidth of the laser, therefore, can be quite large (> GHz!) without risk of exciting unwanted transitions. Previously, multimode lasers have been used in helium metastable atom studies (S. Essabaa, et al., 1991; J. M. Daniels, et al., 1987). However, single mode lasers are simpler to frequency stabilize, and multimode
lasers suffer from competition between the various lasing modes, so the power output at
the desired wavelength may fluctuate unpredictably.

The power necessary to saturate the $\text{He}^2(2^3S) \rightarrow \text{He}^2(2^3P)$ transition is only about 1
mW/cm$^2$, and tests we have performed indicate that metastable beam polarizations > 95%
can be achieved with as little as 20 mW. For optical pumping of metastable helium
beams, then, many of the previous laser systems were satisfactory. However, there are
still good reasons to develop a more powerful laser system. Other experiments,
particularly the construction of a helium metastable atom magneto-optical trap, require
significantly more power to accomplish. Additionally, increasing the laser system output
power by improving the laser efficiency may allow the system to operate with a smaller
pump source (i.e. use of a small frame pump laser when previously a large frame laser
was necessary to obtain the required output power), hence reducing the cost of building
and maintaining the laser system considerably.

B. General Theory

In designing a laser system one must consider many things. Concerns about
output power, wavelength, linewidth, output beam diameter and divergence, stability,
tunability, portability, ease of alignment, cost, and other factors may all have to be taken
into account. The problem is complicated still further by the fact that many of these
characteristics are interdependent, or even worse, conflicting, and that, without
undertaking considerable time, effort, and money, many of the numbers required to make
the necessary calculations can only be approximated.

The starting point is the selection of a lasing medium. A look at Table 1 will
show that few materials have been identified that held promise of generation of 1.083 µm
light. In the present work, which was a continuation of previous research, an LNA crystal
was already available and was chosen for study because of its good conversion efficiency.
Ti:Sapphire, although it exhibits poor fluorescence at 1.083 μm, was chosen by Coherent Laser Group for its greater commercial appeal due to its broad tuning range. Ti:Sapphire has supplanted long wavelength visible and near infrared dye lasers which suffer from turbulence effects, separation, and molecular breakdown of the dye.

The next decision that must be made is that of the type and shape of laser resonator. In standing wave (linear) optical cavities, each longitudinal mode has a unique, sinusoidally varying intensity along the axis resulting in a spatially modulated stimulated emission probability. In solid state lasers the lasing ions are fixed in position, and thus the gain of the laser will vary along the cavity axis. If there is a single mode lasing, there will be regions of gain depletion (antinodes) interspersed with regions (nodes) where gain remains (an effect known as spatial hole burning) (Moulton, 1991a). It is in these regions where gain remains that a second lasing frequency may find sufficient gain to lase, provided its mode also fulfills the boundary conditions of the cavity. So linear laser cavities can be difficult to get to lase single frequency, and do not utilize all of the available gain to produce output power. If operating unidirectionally, ring lasers have traveling wave solutions to the wave equation, and so a single lasing mode, as it travels across the gain medium, can deplete its entire volume. It is easier, therefore, to achieve single-frequency lasing and higher output power with a ring configuration than with a linear laser using the same gain medium, pump power, etc.

The available shapes that ring resonators can take are widely varied (see Figure 2.1). In many laser systems the lenses bracketing the crystal that are used to focus the circulating laser light onto the gain medium are replaced by curved mirrors. An external lens is used to focus the pump laser light through one of the cavity mirrors onto the gain medium. The use of curved mirrors produces an astigmatism of the circulating laser beam because a curved mirror used at oblique incidence focuses ray bundles parallel to the axis of mirror rotation at a different location than those perpendicular to the mirror.
rotation axis. This leads to two different effective focal lengths, $f_{\parallel}$ and $f_{\perp}$, which are related to the actual focal length $f$ of the mirror by (Kogelnik et al., 1972):

$$f_{\parallel} = f / \cos \theta$$
$$f_{\perp} = f \cdot \cos \theta$$ (2-2)

Where $\theta$ is the angle between the incoming ray and the perpendicular to the mirror surface. This astigmatism must be compensated by other elements within the cavity, usually brewster prisms (or brewster-cut faces on the gain medium for solid state media) which have an astigmatism dependent upon their thickness and the index of refraction of the material from which they are made. Quickly one then realizes that small angle reflections at these mirrors are desired to keep the necessary compensation small (it is for this reason that cavity design (A) is rarely utilized).

![Figure 2.1](image-url)  
(A)  
(B)  
(C)  

**Figure 2.1:** Various popular ring laser designs. Four mirror designs shown only. (A) Four mirror square, (B) Figure-eight arrangement popular for use in "swing laser resonators" like the TITAN CW series (Schwartz Electro-Optics), and (C) Four-mirror design favored by Coherent in their 699/899 series lasers.

Consideration of the ABCD matrices (Appendix B) for the three designs shown will all yield the similar results, so to select a particular one other criteria will have to be used such as the angular dependence of the mirror coatings, space for placement of additional optical components (brewster plates, etalons, birefringent filter, etc.), space constraints for the laser itself, astigmatism (if any), and alignment considerations. The (C) design was chosen by Coherent for the 899 because one of its previous systems, the
utilized a similar design and thus greatly reduced the amount of engineering and development necessary for the production of the 899 system. The design (C) was chosen for the ring LNA due to extensive experience with the Coherent 899 ring Ti:Sapphire laser and familiarity with the alignment techniques applied to it.

Ordinarily at this point, a focal spot size would be selected at the gain medium based upon a desired power density within the gain medium, and then a resonator would be designed which would produce that spot size for the circulating laser beam at that location. Then the pump laser beam would be adjusted to match. However, in the case of the LNA laser the greatest concern was damage that might occur to the crystal faces by the focused pump beam. Consequently, the lenses were chosen and placed so that the pump laser achieved a focal spot size that had been found to provide the greatest power density with minimal risk of crystal damage. It is necessary, then, to adjust the round trip distance of the resonator to allow the circulating laser beam waist at the crystal to match that of the pump beam.

As shown in Appendix B, the round trip distance, D, for a laser resonator of design (C) in order to be stable can be calculated using the ABCD matrices given the focal length of the lenses used and their position with respect to the gain medium. This design turns out to be stable for a wide range of round trip distances.

The round trip distance, along with the shape and components of the laser cavity, and the placement of these components within the cavity, determines the beam diameter at all points within the resonator. A detailed study of the fundamental gaussian beam mode (Appendix C) of the cavity, and the necessity that the beam diameter be sufficient to overlap the pump beam waist at the gain medium in order for efficient pump conversion to occur, may place additional restrictions upon the round trip distance. Additionally, the beam waist at other points within the cavity must never diverge to the point that clipping occurs on one of the optical components which make up the cavity.
The calculations show that, with respect to the beam waist constraints, this design is still fairly insensitive to round trip distance, and only repeats the restriction made by the cavity stability criteria in Appendix B. This allows the round trip distance to be determined largely by portability and space constraints, and greatly simplifies the overall ring resonator design.

Note that a ring laser design in and of itself does not determine a preferential direction for the travel of the lasing wave. Since there is no preferential lasing direction within a lasing ring cavity, under ordinary circumstances an open ring laser cavity will either lase in both directions at once, leading to a standing wave mode, or will lase in a single direction which changes with thermal changes within the cavity or mechanical shock to the system. Clearly, as neither result is satisfactory, an optical diode must be included within the cavity, the action of which is to introduce a small loss in one lasing direction with respect to the other, and hence define a preferential lasing direction. An optical diode consists of a length of material, sometimes fused silica, placed in the field of a permanent magnet, and another length of an optically active material, often crystalline quartz. The magnetic field along the first material length, called the Faraday rotator, introduces what is known as the Faraday effect, in which a net rotation occurs in the plane of polarization of a beam passing through it. The key is that the rotation is clockwise for one direction of propagation, and counterclockwise for the other direction relative to an axis defined by the magnetic field. The second material is optically active, which means that a net rotation in the polarization of a beam passing through it takes place, however the sense of rotation is independent of the propagation direction. With the proper choice of material lengths and magnetic field strength, it is possible to produce an arrangement which introduces no net polarization rotation for one direction of propagation, and some finite polarization rotation for the other direction (Figure 2.2). Polarizing elements within the lasing cavity will cause losses to occur each round trip for the direction for which the
polarization has been rotated, and the other direction of oscillation will dominate (Moulton, 1991a). The entire optical diode assembly may be installed at Brewster's angle to minimize insertion losses for the selected propagating beam, though antireflection (AR) coatings on all faces is usually sufficient to allow for normal insertion.

![Graph showing net rotation vs. wavelength]

Figure 2.2: Net rotation in the forward and backward directions for an optical diode as a function of wavelength. The Faraday material is Schott SF-57 glass, while crystalline quartz is used as the optical rotator (Moulton, 1991a).

The final consideration in the design of the laser resonator is that of output laser linewidth. When used in optical pumping experiments, the linewidth of the laser must be such that the transition of interest is excited, while nearby transitions are left unpumped. The output linewidth of the laser (see Appendix D) is dependent upon the single pass gain of the laser medium, the round trip losses, and other quantities for which the values are not readily available. A calculation can be made of an upper limit to the linewidth which depends only upon the round trip distance and the round trip cavity losses (which can be approximated with some degree of accuracy, and depends primarily upon the reflectivity upon the output coupler which represents the largest single loss within the cavity).

Beyond the concerns about the output laser linewidth, the selection of the output coupler reflectivity is based primarily upon two conflicting criteria. The output coupler
can be chosen so as to produce the highest output power from the laser system. Note that this will not necessarily be the output coupler of lowest reflectivity as the curve of output power versus output coupler reflectivity is often shaped like an upside-down u, with a maximum that depends upon the gain medium and the losses within the cavity. Alternately, the output coupler can be chosen with a high reflectivity (typically >97%) to maximize the tuning range of the laser. This also has the advantages that the laser is easier to lase and peak up. Additionally, by keeping a greater fraction of the circulating laser light within the cavity, the laser will be more stable in power and frequency, and less susceptible to feedback from reflections occurring outside the resonator.

The remaining difficulty is that the laser must be made to lase on a single longitudinal mode. In a ring configuration, a laser will lase on modes separated by \(c/D\) in frequency (the separation is \(c/2D\) for a linear, standing wave cavity). For a round trip distance of two meters, this gives a mode spacing of 150 MHz. Depending upon the gain curve for the lasing medium and the laser cavity, lasing may occur on just a few modes or a few thousand. Tuning is achieved using a variety of intracavity elements, the coarsest of which is often the birefringent filter.

The action of a birefringent filter is best understood as a variable-delay retardation plate. Polarized light incident upon a birefringent filter, which is inserted into the laser cavity at Brewster's angle to minimize insertion losses, can be considered in terms of two orthogonal polarization eigenvectors within the filter. These eigenvectors travel through the filter at different speeds, and hence a phase delay is introduced between them. Upon leaving the filter, the beam has experienced a rotation in its plane of polarization which is dependent upon its wavelength. Polarizing elements within the laser cavity will cause round-trip losses except at those wavelengths for which the phase delay is an integral number of \(2\pi\) (i.e. it is not rotated). The relative phase delay between the eigenvectors is
wavelength dependent and can be adjusted by rotating the plate about an axis normal to its surface, hence tuning is accomplished (Preuss and Gole, 1980).

After a birefringent filter is inserted, the laser will still most probably lase on multiple longitudinal modes. Etalons, sometimes several of them, are used to limit lasing to a single mode, and are selected to provide the most power with the smoothest (shortest mode hops) tuning. The transmission properties of a planar etalon are derived in Appendix A, and are given by (Born and Wolf, 1975):

\[
I^{(i)} = \frac{I^{(t)}}{1 + 4R\sin^2(\Delta)/(1-R)^2} \tag{2-3}
\]

\[
\Delta = \frac{2\pi fnd\cos(\Theta)}{c} \tag{2-4}
\]

where \(I^{(i)}\) is the incident light intensity, \(I^{(t)}\) is the transmitted intensity, \(\Theta\) is the angle from the normal for the transmitted beam within the etalon, \(n\) is the index of refraction of the etalon material, \(d\) is the thickness of the etalon, \(R\) is the surface reflection coefficient, and \(f\) is the frequency of the transmitted beam. If an etalon is placed within a cavity which is lasing on several modes, it will cause greater round-trip losses for some modes than for others reducing the number of modes lasing. From (2-3, 4) it can be seen that the angle of the etalon insertion will change which modes experience losses and hence which modes will lase preferentially.

C. The Ring LNA Laser

The round trip distance for stability (Appendix B) given the focal length of the lenses used in the linear LNA is:

\[
31 \text{ cm} \leq D \leq 397 \text{ cm}
\]

Gaussian beam waist considerations show that a round trip distance of approximately two meters provides a beam waist at the crystal which overlaps and
matches well that of the pump laser light, while the circulating laser beam waist does not clip on any of the cavity components. Using these figures, an output beam diameter of about 1.2 mm is calculated with a divergence angle of 1 mrad.

Due to the fact that fused silica tends to become absorptive at wavelengths greater than 900 nm, the optical diode employed (custom, Optics for Research) utilizes a material known as TGG (Terbium Gallium Garnet) as the Faraday rotator. TGG does not absorb in the near IR, and it also exhibits a strong Faraday effect, which allows a shorter piece to be used. A half-wave plate mounted in the optical diode assembly can be adjusted to zero the polarization rotation for the preferred lasing direction. With proper adjustment of the half-wave plate, this optical diode produces a 4° rotation in the plane of polarization in one direction of travel, with no net rotation occurring in the other, which is sufficient to maintain unidirectional lasing.

There has been no special attempt made to isolate the laser resonator or its components from mechanical vibrations, so a fast jitter ~ few MHz. is to be expected. As is shown in Appendix D, the upper limit to linewidth is $7.2/D(m)$ MHz given a 95% reflective output coupler. For a round trip distance of 2 m, the upper limit on the output laser linewidth is therefore 3.6 MHz. This is on the order of the mechanical jitter and is certainly an acceptable value for our applications.

The output coupler (95% reflective) was selected from an available assortment of 80%, 85%, 90% and 95% reflective mirrors and provided the greatest output power.

For LNA, there are two regions of gain, both of which are relatively narrow, centered at 1.054 µm and 1.082 µm. Attempts have been made in the past to remove the 1.054 µm lines, which exhibit higher gain in comparison to the 1.083 µm lines, by using an output coupler or mirrors which have a lower reflectivity at 1.054 µm. The results have been unsatisfactory, owing to the closeness of 1.054 µm and 1.083 µm and the comparatively higher gain at 1.054 µm. Further study has shown that a two plate
birefringent filter can be used to eliminate the 1.054 μm lines with, for proper alignment, minimal losses at 1.083 μm.

Upon insertion of the birefringent filter, the lasing is restricted to several dozen lines. Etalons were selected, largely by trial and error, to obtain the most single-mode power with the smoothest (shortest mode hops) tuning. Insertion of the first, thin etalon (uncoated, FSR ~ 900 GHz.) resulted in only two longitudinal modes. Use of a second, thicker etalon (50% reflective coatings, FSR ~ 50 GHz.) in the laser cavity resulted in single frequency operation.

D. The CR899-21 Ti:Sapphire Laser

(Much of the information about the 899 is proprietary to Coherent and is unavailable.)

Choice of the round trip distance is somewhat more restricted because of the necessity of compensating the astigmatism associated with oblique incidence upon the curved cavity mirrors using the brewster cut Ti:Sapphire crystal, and a round trip of 1.67 m was chosen. The output beam diameter can be approximated as 1mm with a divergence (full angle) of 1 mrad.

The optical diode is fabricated from TGG as discussed above, and also achieves approximately a 4° rotation.

The entire laser resonator is constructed upon a stainless steel bar for rigidity, but is not really vibrationally isolated from its environment. When operating under the locking electronics of the laser system, a fast jitter of 3-5 MHz is specified by Coherent.

The output coupler is proprietary, but is approximately 98.5%. This reflectivity was chosen, probably, to allow the customer an easier time of lasing and peaking the system up, but reduces the possible output power of the system considerably.

Ti:Sapphire, owing to its broad fluorescence spectrum, will have thousands of modes, 180 MHz apart given the round trip distance above, lasing in an open cavity. The
laser is again tuned and single-frequency operation maintained by a (three plate) birefringent filter, and a combination of thick (FSR ~ 10 GHz) and thin (FSR ~ 220 GHz) etalons.
Chapter Three
The Ring Laser Systems

A. The Ring LNA Laser

Developed in France and the Soviet Union as an alternative to Nd:YAG (Bagdasarov et al., 1983), LNA is a material that exhibits laser action on tunable bands centered at 1.0545 μm and 1.0820 μm (Scheerer et al., 1986). The absorption and fluorescence spectra are shown in Figure 3.1a,b.

The present laser is shown schematically in Figure 3.2. The central component of the laser is a c-axis cut LNA crystal 5 mm in diameter and 6 mm long. The ends of the crystal are antireflection (AR) coated and it is mounted in a water cooled copper block. The crystal is excited by the 514.5 nm output of an Argon ion laser that enters the cavity through a dichroic mirror. Due to its short length, however, the crystal absorbs only ~65% of the incident pump radiation. The laser cavity is defined by four planar mirrors, and the circulating beam (and the pump radiation) is focused at the center of the LNA crystal using a pair of 7.5 cm focal length AR-coated fused quartz lenses. The lenses are fixed in z-axis mounts to allow precise adjustment of the positions of the lenses with respect to the crystal. Coarse tuning of the laser is provided by a two-element birefringent filter. Fine tuning is achieved using a pair of solid fused-quartz etalons: the first is uncoated and has a free spectral range (FSR) of ~900 GHz, the second has 50% reflective coatings on each face and a FSR of ~50 GHz. Unidirectional lasing is established by use of an optical diode comprising an AR-coated Terbium Gallium Garnet slab and half wave plate.

Electronic stabilization and tuning of the cavity is obtained through three active elements. Firstly, the lower high reflector is mounted on a piezoelectric translator (PZT) which allows for fine tuning by varying the cavity length and can rapidly (~ kHz
Figure 3.1a: LNA Absorption Spectrum (Vansteenkiste, 1989).

Figure 3.1b: LNA Fluorescence Spectrum (Vansteenkiste, 1989).
Figure 3.2: Schematic Layout of the LNA Laser
frequency response) correct changes induced by vibrations. However, the limited travel of the PZT (±1 μm) necessitates the use of other tuning elements. A galvanometer-driven 2.5 mm thick fused quartz plate is inserted into the cavity near Brewster's angle (called the Brewster plate). Rotation of this plate about its vertical axis changes the optical path length through it. In this way it is able to compensate for larger, but slower, changes in the cavity length. As the Brewster plate reaches the end of its travel, the final tuning element is used. The coated etalon is mounted in such a way as to allow rotation about its vertical axis by the voice coil of a small loudspeaker. Feedback signals cause the next tuning element to move when the previous element has reached the end of its tuning range. The adjustment of these three elements provides a stabilized, single-frequency tunable laser about 1.083 μm. Residual pump light present in the output beam is removed using a Schott RG 850 filter.

The generation of an error signal to control the active cavity elements is accomplished using a temperature-stabilized reference cavity (Burleigh Instruments Model CFT 25 confocal Fabry Perot etalon with a finesse of ~5 and FSR ~3 GHz.). Transmission through the reference cavity is frequency dependent, so laser stabilization can be achieved simply by sending a small fraction of the output beam through the reference cavity, and adjusting the laser so as to keep the transmission constant. A power reference photodiode is included to differentiate changes in laser power, which would also cause a change in the power transmitted through the reference cavity, from true frequency drift. Transmission of the reference cavity is set at 50%, so frequency drift in one direction causes an increase, and in the other direction causes a decrease, of the transmitted power. In this way, the direction of the laser drift is indicated, and hence the direction of tuning necessary to return the laser to its locking frequency. Drifts associated with the reference cavity result in changes in the output frequency of typically ≤ 5 MHz/hr. These changes, however, are sensed and corrected using a technique that
employs a scanning Fabry-Perot etalon and stabilized Helium-Neon laser, called Superlock, thereby reducing long-term output frequency drifts to ≤ 1 MHz/day (Lindsey et al., 1991).

Figure 3.3 shows the single-frequency 1.083 μm output power obtained with a 95% reflective output coupler as a function of pump power. The laser was routinely operated with 5 W pump power, sufficient to provide output powers of ~330 mW.

![Graph](image)

**Figure 3.3:** Output laser power versus input pump laser power.

The laser has also been tested with the coated solid etalon replaced by a planar piezoelectrically-driven air-gap etalon (Burleigh Instruments model TL-15) having 50% reflective coatings (the outermost surfaces are AR coated) and a FSR of ~150 GHz. Use of this etalon results in a small decrease, ~10%, in output power but, because it eliminates the need for the voice coil actuator, also reduces sensitivity to microphonic noise.

**B. The CR899-21 Ti:Sapphire Laser**

In June 1982, before the Twelfth International Quantum Electronics Conference in Munich, Peter Moulton of Lincoln Laboratory reported the operation of a Ti:Al₂O₃ laser. Ti:Sapphire proved to be an extremely versatile solid state laser media because of its
broad tuning range (Figure 3.4a), as well as its strong absorption of the all-lines output (488-514nm) of an Argon ion laser (Figure 3.4b) (Moulton, 1986). A modified CR899-21 Ti:Sapphire ring laser designed by Coherent Laser Group is used in the present work and is optimized for operation at longer wavelengths.

The design of the 899 lasing cavity, shown in Figure 3.5, is also uses a four-mirror ring configuration (input dichroic mirror M1, upper fold mirror M5, output coupler M4, and piezoelectric translator-driven mirror M3 also known as the fast tweeter). Pump optics P1, P2, P3 are used to align the input pump beam through lens L1 to be focused onto the crystal.

The tuning elements of the 899 are similar to those used in the LNA laser. A birefringent filter (three plate with thickness ratios 1:4:16) is utilized for course tuning along with a thin etalon (FSR ~220GHz) which is sealed within the intracavity assembly and rotated electronically about its vertical axis. The active tuning elements consist of a fast tweeter M3, a two-piece air-gap thick etalon for which the air gap separation is controlled by a PZT (FSR ~10GHz), and twin Brewster plates. An error signal is generated using a reference cavity (finesse ~3, FSR=1GHz) and a power reference photodiode powered by a small fraction of the output beam, much in the same way as the ring LNA laser. The drift of this reference cavity has been shown to be > 20 MHz/hr, however Superlock can be applied to this system as well, reducing this drift to ≤ 1 MHz/day. The fast tweeter corrects fast frequency fluctuations, while the motion of the Brewster plate allows the PZT to remain near the center of its range. When it is necessary to move to the next longitudinal mode, the air gap etalon moves, and the fast tweeter and Brewster plate track to the new cavity mode. The air gap is dithered continually, with a circuit which monitors the output power of the laser, to keep the gap optimally adjusted.

Certain changes have been made to allow the present 899 greater efficiency when lasing in the near IR. The main emphasis in these changes has been to minimize the
Figure 3.4a: Ti:Al$_2$O$_3$ Fluorescence Spectra (Moulton, 1986).

Figure 3.4b: Ti:Al$_2$O$_3$ Absorption Spectra (Moulton, 1986).
Figure 3.5: The 899 Ti:Sapphire Ring Laser (High Power Configuration)
round trip losses of the lasing cavity. As discussed in chapter three, the optical diode, which represents the greatest optical path length within the cavity with the exception of the Ti:Sapphire crystal itself, has been constructed with a Faraday rotator made from TGG instead of fused silica to reduce absorptive losses. The etalons and Brewster plates, which do not represent very long path lengths, are still made of fused silica because of the extreme cost associated with using TGG for all these elements.

Ordinarily, a single Brewster plate is used in the 899 system, and it is vertex mounted near output coupler M4. The vertex mounted Brewster plate is impinged upon by two beams, one from upper fold mirror M5, and one from tweeter mirror M3. As such, it is clearly impossible for the Brewster plate to be at Brewster's angle for both beams. This would introduce reflection losses. In this system, two Brewster plates are inserted along the beam line from the output coupler M4 to the tweeter mirror M3, both nominally at Brewster's angle (Figure 3.6). Two Brewster plates can achieve greater path length correction with a smaller deviation from Brewster's angle than is possible with the single plate arrangement.

![Figure 3.6](image)

**Figure 3.6**: Brewster plate configurations. (A) twin Brewster plates rotated in opposite directions to eliminate beam offset and reduce angular adjustment necessary for tuning, and (B) a single vertex mounted Brewster plate (developed by Coherent for the 699 model). (Moulton, 1991b)

Finally, the Ti:Sapphire crystal used in this system has been selected as one which exhibits increased infrared fluorescence.
The tuning curve for the present laser when using optics optimized for long wavelength operation (known as the long wavelength set) is shown in Figure 3.7. The laser produces 300 mW of 1.083 μm light when pumped with 21 W of all-lines Argon ion laser light.

![Graph](image)

**Figure 3.7:** Ti:Sapphire Tuning Curve (long wavelength optics set)
Chapter Four

Ring Laser Applications

A: Optical Pumping

In 1950, resonance radiation was used to selectively populate certain \( m_J \) states of mercury (Brossel et al., 1950) to achieve a population distribution which was different from that normally found at equilibrium. This process became known as optical pumping, and soon afterwards it was applied to helium in the \( 2^3S_1 \) metastable state (Franken and Colegrove, 1958). The use of unpolarized \( 2^3S_1 \leftrightarrow 2^3P_{0,1,2} \) resonance radiation excites the atoms to the \( 2^3P \) states, which subsequently decay back to the \( 2^3S_1 \) level. Spontaneous decay back to the \( 1^1S_0 \) level is forbidden by the electric dipole transition selection rule \( \Delta S = 0 \) (i.e. the \( 2^3S_1 \) level is the ground state of the triplet system). This accounts for the long lifetime of the \( 2^3S_1 \) state (~10^4 sec) (Corney, 1977).

It is clear that after repeated excitation and decay cycles the \( m_J \) level (where \( m_J \hbar \) is the projection of the atomic angular momentum on the \( z \)-axis, which is defined as parallel to the direction of propagation of the optical pumping radiation) and which has the smallest absorption probability, will have the highest population. In the present work, circularly polarized laser radiation is used to produce beams of He(\( 2^3S \)) metastable atoms which are all in either the \( m_J = +1 \) or in the \( m_J = -1 \) state. The polarization \( (P_z) \) of the resulting beam is defined as:

\[
P_z = \frac{N_{+1} - N_{-1}}{N_{+1} + N_{-1} + N_0}
\]

where \( N_{+1}, N_{-1}, \) and \( N_0 \) are the populations in the \( m_J = +1, -1, \) and 0 states respectively.

The technique is illustrated in Figure 4.1. At equilibrium, the various He(\( 2^3S_1 \)) \( m_J \) levels will all be populated equally. Illumination with right hand circularly polarized (RHCP) 1.083 μm \( 2^3S_1 \leftrightarrow 2^3P_2 \) resonance radiation excites transitions subject to the
Figure 4.1: Partial term diagram for helium showing the $m_j$ magnetic sublevels of the $2^3S_1$ and $2^3P_{0,1,2}$ states. The dashed arrow indicates a transition by the absorption of a RHCP photon, and the solid arrows denote subsequent spontaneous decay channels. Air wavelength values indicated.
selection rule $\Delta m_j = +1$. One such transition is shown by the dashed arrow. Subsequent spontaneous decay back to the $2^3S_1$ level is governed by the selection rule $\Delta m_j = 0, \pm 1$ represented by the solid arrows. It is evident that through this excitation/deexcitation cycle atoms have been transferred from the $m_j = -1$ state to the $m_j = 0, +1$ states (in the absence of collisions or other depolarizing effects). Repeated cycles result in all the atoms being pumped into the $m_j = +1$ state. Because the helium atoms are in the $2^3S_1$ state, $m_j = m_S$ (where $m_S h$ is the projection of the spin angular momentum of the electrons along the z-axis), so the optical pumping has resulted in helium metastable atoms which are electron spin polarized. Reversing the sense of circular polarization of the optical pumping radiation results in atoms which are electron spin polarized in the opposite direction. Any effects from instrumental asymmetries can be removed in this way.

A good test of the stability of a laser is to demonstrate its ability to provide optical pumping of a collimated He($2^3S$) atom beam for prolonged periods of time. This test was undertaken using an apparatus described in detail elsewhere (Hart et al., 1989) (see Figure 4.2). Briefly, a beam containing He($2^1S$) metastable atoms is first formed by coaxial electron impact excitation. The $2^1S$ atoms in the beam are removed from the beam by irradiating it with 2.06 $\mu$m light from a helium discharge lamp that excites transitions of the type $2^1S \rightarrow 2^1P \rightarrow 1^1S$. The $2^3S$ atoms are not similarly deexcited as the $2^3S$ level is the ground state of the triplet system. The $2^3S$ atoms are then optically pumped using circularly polarized 1.083 $\mu$m radiation from the laser. The laser radiation is incident parallel to a small (~5 gauss) magnetic field applied perpendicular to the $2^3S$ beam axis that defines a convenient quantization axis. Because of Zeeman splitting due to the magnetic field applied to the optical pumping region and the negation of the Doppler effect when transverse optical pumping, the laser would have to be retuned slightly to obtain optimized optical pumping when changing the sense of circular
polarization of the pumping radiation. While this could be accomplished easily with an external input into the superlock control electronics, another option, which we employed here, is to dovetail the beam with a lens. The resulting increase in the effective Doppler linewidth then negates the need to retune the laser when changing the sense of circular polarization of the pumping radiation. The laser illuminates the atom beam for a length of several centimeters. A beam stop was used to eliminate depolarization due to scattered laser light, but it was determined that it was unnecessary as very little light was backscattered off of the diffusion pump cold cap at the bottom of the optical pumping chamber. Beyond the optical pumping region is a second vacuum chamber which contains equipment for preparation and characterization of the target surface as well as a Mott polarimeter and energy analyzer to study the electrons ejected from the surface upon collision with the metastable atoms. In studying optical pumping the surface is moved out of the beam path so that the $2^3S_1$ atom polarization can be determined by spatial separation of the $M_J$ ($M_S$) components using a Stern-Gerlach (SG) analyzer. The spatial distribution of metastable atoms at the output of the SG analyzer is measured using a movable channeltron. Neutral density filters as high as 80% absorption could be inserted into the laser beam without decreasing the metastable polarization, indicating that the transition is well saturated by the 300 mW output power provided by either laser.

Figure 4.3(a) shows the spatial profile at the output of the SG analyzer in the absence of optical pumping. SG profiles obtained following optical pumping on the $3S_1 \rightarrow 3P_2$ ($D_2$) transition with right and left-hand circularly polarized light from either laser are shown in figures 4.3(d) and 4.3(e). 4.3(b),(c) are obtained with optical pumping using a rf Helium discharge lamp and are included for comparison. It is apparent from Figure 4.3 that the ring LNA laser can provide very effective optical pumping with beam polarizations approaching 100%. Indeed, the small remaining $M_J=0$ feature may comprise residual $2^1S$ atoms in the beam, or may result from imperfect circular
Figure 4.3: Helium Stern-Gerlach Profiles. (a) is unpumped, (b) and (c) are pumped with right- and left-hand circularly polarized light from a discharge lamp, and (d) and (e) are typical profiles achieved when pumping with right- and left-handed circularly polarized light from either the ring LNA or Ti:Sapphire laser.
polarization of the optical pumping radiation, or from misalignments and inhomogeneities of the magnetic field in the optical pumping region. This beam polarization could be routinely maintained for periods of many hours without need to adjust the laser.

B. Penning Ionization

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 (PI) in collisions involving He(2^3S) atoms and some atomic or molecular target M (Yencha, 1984):

\[ \text{He}(2^3S) + M \rightarrow \text{He}(1^1S) + M^+ + e^- \] (4-2)

Analysis of the energy distributions of product electrons resulting from interactions such as (4-2) using a potential curve model shows that PI can often be described in terms of a direct transition from the covalent He(2^3S) + M entrance potential to the He(1^1S) + M^+ exit potential. Because neither potential is strongly dependent upon the internuclear separation, ionization via such a "covalent" channel results in a narrow distribution of Penning electron energies. For targets with a positive electron affinity, however, ionization may be preceded by an adiabatic transition from the covalent entrance potential into a strongly-attractive He^+ + M^+ ionic potential. Because this potential changes rapidly with internuclear separation, ionization via this "ionic" channel leads to a broad distribution of energies.

The apparatus used in spin-dependent PI studies has been described elsewhere (Rutherford et al., 1990) and is shown in Figure 4.4. Helium entering the flow tube is excited by microwave discharge using a nozzle geometry which provides excitation with a high triplet (2^3S) to singlet (2^1S) ratio. A Y-shaped flow tube is used to prevent illumination of the optical pumping region with unpolarized 1.083 µm radiation from the microwave discharge. Ions and electrons produced during the excitation process diffuse rapidly into the walls of the flow tube where they recombine. The diffusion process is
Figure 4.4: Schematic Diagram of Flowing Afterglow Apparatus.
enhanced using an rf heating coil which is wound around the outside of the flow tube. The flow tube is evacuated by a 500 l/s Roots pump.

Optical pumping occurs in an electrically-isolated aluminum section equipped with planar windows which is connected to the flow tube. The He(2\textsuperscript{3}S) are optically oriented by the absorption of circularly polarized 1.083 \( \mu \)m \( (2^{3}S \leftrightarrow 2^{3}P) \) radiation incident perpendicular to the helium flow and parallel to an external magnetic field \( \sim 1 \) gauss that defines a quantization axis. The 1.083 \( \mu \)m light is circularly polarized using a quarter wave plate. The sense of circular polarization, and hence the magnetic sublevel that is populated, is reversed by rotating the quarter wave plate by 90°.

Target gas is injected near the extraction aperture through a fine hypodermic needle. Previous studies (Ratliff \textit{et al.}, 1989) have shown that, with the exception of O\textsubscript{2}, and NO, or any open shell target, the electron energy distribution (EED) and polarizations are insensitive to target gas flow rate over a wide range. Upon collision of the He(2\textsuperscript{3}S) atoms with the target, electrons are produced that diffuse to the walls of the flow tube where some pass through the extraction aperture. These electrons are focused into a beam by a series of electrostatic lenses and pass through a hemispherical energy analyzer to a Mott polarimeter (Zhang \textit{et al.}, 1991). The resolution of the hemispherical analyzer (~ 0.4 eV) was chosen to allow study of the different features in the Penning electron spectra, while at the same time allowing transmission of relatively high electron currents to facilitate polarization measurements. For the present geometry, some source electrons can travel down to the extraction region where they provide a small contribution to the ejected electron signal at energies \( \leq 0.5 \) eV, so data analysis in this region is not possible.

The initial polarization of the He(2\textsuperscript{3}S) atoms is obtained by measuring the polarization of electrons produced via Penning Ionization of argon gas. Previous studies (Keliher \textit{et al.}, 1975) have shown that PI reactions with Ar proceed through the covalent
channel with full conservation of the spin angular momentum, and hence may be written as:

\[ \text{He}(2^3S) \uparrow \uparrow + \text{Ar}(1^1S_0) \downarrow \downarrow \rightarrow \text{He}(1^1S) + \text{Ar}^+ \left(2^2P_{\frac{3}{2}, \frac{1}{2}} \right) \uparrow + e^- \uparrow \]  \hspace{1cm} (4.3)

Therefore, the polarization of the ejected electrons is the same as that of the incident He(2^3S) atoms. The polarization was typically measured as \( \sim 0.7 \), and could be reliably maintained for periods of many hours.

In the absence of a target gas, a significant extracted electron signal was observed. This signal is comprised of electrons ejected by metastable impact with surfaces in the vicinity of the extraction aperture. It has been found that these electrons have a broad energy distribution with a polarization typically \( \sim 70\% \) of the He(2^3S) atoms (Hart et al., 1989). In the presence of a target gas this signal is quite small because most metastable atoms are deexcited in collisions with the target gas. Therefore, contributions from the surface ejected electrons are unimportant except in energy regions where the Penning electron signal is small.

While we have studied many gases using this apparatus, the data for CO and NO\(_2\) are presented (Figures 4.5a,b) because they illustrate many of the features interesting to study. Also presented in the figures are EEDs measured (with higher energy resolution) by previous researchers (Hotop et al., 1979). The general features of the current work and earlier results are in good agreement, demonstrating that electrons can be extracted from the afterglow without altering their energy significantly, although the relative extraction efficiency appears to decrease at higher electron energies.

The EED for CO (Figure 4.5a) (Rutherford et al., 1992) comprises a series of sharp features, which correspond to ionization into \( \text{X}^2\Sigma^+, \text{A}^2\Pi \) and \( \text{B}^2\Sigma^+ \) states of the CO\(^+\) ion, suggesting ionization via the covalent channel (Y. Harada, et al., 1983). The polarization of the \( \text{X}^2\Sigma^+ \) feature is equal to that of the 2^3S atoms. The polarization of the
Figure 4.5: Electron energy distributions and polarization profiles measured following PI reactions with (a) CO and (b) NO₂. Diamonds with error bars, electron polarizations (relative to the He(2³S) polarization; open circles, measured energy distributions; solid line, energy distributions obtained by H. Hotop et al., 1979.
(smaller) A^2Π feature appears to be a little lower, but this may be attributed to contributions to the extracted electron signal from surface ejection. The data thus suggests that spin is conserved in PI reactions with CO and that ionization occurs via an Auger-type process in which an electron of the appropriate spin from the target molecule tunnels into the 1s↓ hole in the 2^3S atom with simultaneous ejection of the 2s↑ electron.

The EED for NO₂ (Figure 4.5b) (Rutherford et al., 1993) comprises a broad relatively featureless background associated with ionization via ionic channels (NO₂ has a sizable electron affinity ~2.4 eV) superimposed upon which are a number of sharp peaks corresponding to ionization from the covalent entrance channel into 3B₂(4b⁻¹), 3A₂(1a⁺), and 3B₂(3b₂) states of the NO₂⁺ ion (the NO₂ orbital from which the electron is removed is indicated in brackets) (W. Goy et al., 1983; O. Leisin et al., 1985). Since covalent ionization can only occur at relatively small separations, this requires that a fraction of the collision partners survive the crossing with the He⁺ - NO₂⁻ ionic potential. This is to be expected because the collision partners, He(2^3S) and NO₂(2A₁), can form either doublet or quartet spin states whereas the He⁺(2S) - NO₂⁻(1A₁) system allows only doublet spin states. Thus reactions via the ionic channel are spin forbidden for the quartet entrance channel. Spin conservation, however, requires that (covalent) reactions via the quartet channel produce triplet NO₂⁺ ions, as is observed. The large polarization measured in the vicinity of the 3B₂(4b⁻¹) and 3A₂(1a⁺) features is consistent with ionization via the covalent channel, although the polarization may be degraded somewhat as the result of exchange (NO₂ is an open-shell molecule). The local maximum in polarization observed at energies below ~2 eV may be attributed to contributions to the total electron signal associated with population of the NO₂⁺ 3B₂(3b₂) and (possibly) 3B₁(1b₁) and 3A₁(5a₁) states via the covalent channel.

The pronounced decrease in electron polarization observed at energies below ~4.5 eV coincides with the increase in electron signal attributed to ionization via the ionic
channel. Because electron transfer must form NO$_2^-$ ions in the $^1A_1$ state, autoionization of the resulting He$^+$ - NO$_2^-$ collision complex may the be accompanied by ejection of either an $\uparrow$ or $\downarrow$ electron. Assuming that each is equally probable, ionization via the ionic channel will give electrons with zero polarization. This would explain the very low polarization measured at energies near 3 eV where there is only a small contribution to the total electron signal from the covalent channel.

This data demonstrates the usefulness of spin-labelling techniques for probing the dynamics of PI reactions.

C. Spin Polarized Metastable Deexcitation Spectroscopy (SPMDS)

Electron spin labeling techniques provide a powerful method with which to probe the dynamics of He(2$^3$S) atom deexcitation at surfaces. The apparatus used is shown in Figure 4.2, and has already been described.

Deexcitation of the incident He(2$^3$S) atoms occurs through two possible channels dependent upon the surface work function and type (Figure 4.6). One channel is actually a two-step process. In the first step, the 2s electron of the helium atom tunnels into an unoccupied surface state, resulting in Resonance Ionization (RI). In a second step, termed Auger Neutralization (AN), a ($\downarrow$) electron from the surface tunnels into the helium 1s orbital, leaving the atom in the ground state, with the possibility of the ejection of an electron from the surface. This deexcitation channel will result in electrons which are spin-polarized (for nonmagnetic surfaces) only to the extent that there is a correlation between the spins of the two electrons involved in the Auger process. In the absence of unoccupied surface states which are degenerate with the excited electron state of the metastable atom RI will be suppressed, and deexcitation occurs via a second channel. In the Auger Deexcitation (AD) process a ($\downarrow$) electron from the surface tunnels into the helium 1s orbital with the ejection of the 2s electron (again leaving the helium atom in the ground state). Note that electrons ejected via this channel will be spin-polarized, with a
polarization equal to that of the incident metastable atoms. Analysis of the ejected electron energy alone would make it difficult to distinguish between RI + AN and AD because the ionization energy of the metastable and the surface work function are effected by the atom-surface interaction.

![Diagram](image)

**Figure 4.6:** (a) RI + AN and (b) AD processes with spin labels

Our use of this apparatus was modified to provide still further information about the deexcitation reaction dynamics. Turning off the quench lamp allows He(2$^1$S) atoms to continue down the beam line and interact with the surface. Transverse illumination of the beam at the target surface with a 1.083 µm laser allows saturation of the 2$^3$S $\rightarrow$ 2$^3$P transition, permitting study of the interaction of He(2$^3$P) atoms with surfaces to be studied.
Energy distributions of electrons ejected from an atomically clean Cu(100) surface by incident helium $2^3S, 2^1S$ ad $2^3P$ atoms are shown in Figure 4.7 (D. M. Oro et al., 1992b) along with the polarization of the electrons ejected during He($2^3S$) - surface interactions (expressed as a percentage of the initial metastable beam polarization). It is evident that, to within experimental error, the electron energy distributions are identical for all three species. This can only be explained if deexcitation occurs exclusively through RI + AN for all species, i.e. each incident atom is converted into a He$^+$ atom prior to electron ejection occurring.

![Figure 4.7](image_url)

**Figure 4.7:** EEDs resulting from deexcitation of He($2^3S$) atoms (---), a He($2^3S$)/He($2^3P$) mixture (---), and He($2^1S$) atoms (...) at an atomically clean Cu(100) surface. Dark circles with error bars are the ejected electron polarizations measured in earlier studies using polarized He($2^3S$) atoms.

However, the observed polarization requires that the electrons involved in the AN process tend to have antiparallel spins. The observed spin correlation is quite large, especially at the highest ejected electron energies for which both electrons must originate near the Fermi level. Model calculations (F. B. Dunning and P. Nordlander, in press)
suggest that this can be explained by considering the local perturbation in the surface electronic structure induced by the presence of the (polarized) He$^+$ ion. The calculated densities of states are spin dependent and exhibit sharp resonances near the Fermi surface.

We have further applied spin polarization techniques to the study of He(2$^3$S) deexcitation at a Xe film adsorbed on a cooled Cu(100) substrate (D. M. Oro et al., 1994). The data (Figure 4.8) contain two higher-energy peaks similar to those observed in gas-phase PI indicating that ejection results, in part, from AD, i.e. surface Penning ionization (SPI). These correspond to ionization into the $^2$P$_{1/2}$ and $^2$P$_{3/2}$ states of the product Xe$^+$. 

![Figure 4.8: EEDs resulting from the deexcitation of He(2$^3$S), He(2$^1$S), and He(2$^3$P) at a cooled Cu(100) surface exposed to 30 L of Xe. The ejected electron polarizations measured with incident polarized He(2$^3$S) atoms are indicated by the dark circles with error bars. The electron polarization is expressed as a percentage of that of the incident He(2$^3$S) atoms.](image)

ion. The separation in the energy of the peaks is similar to that observed in gas-phase PI, but their absolute energies are significantly higher, indicating that the binding energy of the atomic 5p$^6$ electrons is significantly reduced at the surface. The energy of these features were found to decrease with increasing film thickness, indicating that the binding
energy reduction is due to image charge effects associated with the substrate and to
dielectric screening of the product Xe\textsuperscript{+} ion by neighboring Xe atoms.

However, there is also a lower energy feature that has no analog in gas-phase PI
spectra. Additionally, the energy of this feature does not vary with incident species
showing that it does not result from AD. The experiment was repeated using a Au(100)
substrate, a cesiated Cu(100) substrate, and an Ar film upon Cu(100) substrate. The low
energy feature was found to have no significant substrate dependence. Because the
increased internal energy associated with incident 2\textsuperscript{1}S and 2\textsuperscript{3}P atoms does not result in
any significant change in the profile or position of the low-energy feature, it might be
due to AN of He\textsuperscript{+} ions formed through RI. RI, however, requires the availability of
empty levels at the surface resonant with the excited helium electron. Solid xenon has
positive electron affinity and inverse photemission studies show the presence of
unoccupied levels ~ 1.5 ev below the vacuum level (K. Horn et al., 1987). As an excited
helium atom approaches the surface, image charge interactions and hybridization effects
raise the electronic energy levels relative to the vacuum level (F. B. Dunning et al.,
1991). RI is consistent with the observation that the size of this feature increases as the
internal energy of the incident atoms, and hence the overlap with available empty states at
the surface, increases.

The Xe film provides an unusual example of a surface at which RI and AD occur
in parallel with comparable rates. At clean, high work function metal surfaces where
there is a high density of unoccupied levels electron ejection occurs exclusively through
RI + AN (D. M. Oro et al., 1992b). For thick films of many spin-singlet gases, only AD
(SPI) is observed (W. H. Butler et al., 1992; D. M. Oro et al., 1992c). Two factors may
contribute to the balance between RI and AN (SPI) observed for a Xe film. The
unoccupied states in the film may be sufficiently close to the vacuum level that the
separation between the incident atoms and the surface must become very small before
energy resonance is obtained, thereby allowing AD (SPI) to become competitive. Alternately, the density of unoccupied levels may be sufficiently low as to limit the RI rate and permit AD (SPI) to compete effectively.

Our measurements have established polarized helium metastable atoms as an extraordinarily sensitive probe of the surface electronic and magnetic environment and of the marked changes that can occur in the presence of adsorbed atoms.

D. Absolute Calibration of a Mott Polarimeter

Mott polarimeters are used in many areas of physics to measure the spin polarization of electrons (J. Kessler, 1985). They function by exploiting the left-right scattering asymmetry which occurs when polarized electrons are scattered at high energy from high-Z nuclei in a target foil. The asymmetry is the result of the interaction between the electron’s spin magnetic moment and the transformed magnetic field in the electron’s rest frame due to the electric field of the scattering nucleus, called the spin-orbit effect.

Traditionally, the scattering asymmetry is related to the incident electron’s spin polarization via an asymmetry function, also known as the Sherman function. The Sherman function can be computed for relativistic electrons scattering from point Coulomb fields of gold or other nuclei. However, the fact that electrons scattering from a target foil can undergo multiple scattering events before being detected degrades the scattering asymmetry, and the effective Sherman function is often less than the theoretical value.

To compensate, two techniques have been employed. In the first, the scattering asymmetry is measured using foils of varying thickness, and then extrapolated to zero thickness. This value is then normalized to the theoretical result. There is, however, disagreement as to the best method for extrapolating to the zero thickness value. Alternately, the Sherman function can be measured for various inelastic energy loss windows for the scattered electrons. The motivation for this method is the expectation
that multiple scattering events lead to electron energy loss. The experimental results are then extrapolated to zero energy loss and normalized to single atom theory. This method also suffers from the uncertainty in the extrapolation technique.

A third option, which is presented here (D. M. Oro et al., 1992a) uses a Mott polarimeter to measure the scattering asymmetry of a beam of electrons whose polarization is known independently through some other method. From this the Sherman function can be calculated, and hence the polarimeter absolutely calibrated. Looking again at the Xe data, Figure 4.8 shows that the ejected electrons associated with the high-energy SPI peak have a polarization equal to that of the incident metastable atoms which can be measured using the SG analyzer. The electrons in this feature then provide a polarized electron source of accurately known polarization, and measurement of the scattering asymmetry allows computation of the Sherman function appropriate to the polarimeter directly without the need for theoretical calculations or extrapolation.

Gas phase PI reactions in which electrons of known polarization can be obtained from spin-polarized metastable atom - target gas interactions can also be used to calibrate Mott polarimeters. However, SPI results in higher electron currents than can be obtained through gas-phase PI, and this leads to lower statistical uncertainties. Additionally, the high beam polarization that can be obtained using the present lasers for optical pumping reduces the effects of possible systematic errors associated with measurement of the $2^3S$ polarization using the SG analyzer.

**E. Cooling and Trapping He($2^3S$) Metastable Atoms**

The high power produced by the ring lasers allows for the construction of a magneto-optical trap (MOT) for He($2^3S$) metastable atoms. Trapped metastable atoms permits a number of interesting studies. Among them is direct measurement of the He($2^3S$) natural lifetime. Theoretical calculations suggest that He($2^3S$) decays via a relativistic magnetic dipole transition, and that the radiative lifetime is on the order of $10^4$
seconds. Other studies could include spin-polarized $^{4,3}\text{He}(2^3S) - ^{4,3}\text{He}(2^3S)$ and resonantly-enhanced $^{4,3}\text{He}(2^3S) - ^{4,3}\text{He}(2^3P)$ Penning reactions in the quantum collision regime ($^4\text{He}$ is a Boson while $^3\text{He}$ is Fermion; dramatic differences are expected).

The theory of the MOT in one dimension is shown in Figure 4.9. The Zeeman sublevels of a two-level ($J=0$ and $J=1$) system in a linearly varying magnetic field ($B(z)=bz$) are represented by the solid lines. The laser frequency, represented by the long, dashed line, is detuned below the zero-field resonance by $\delta$. For a slowly moving atom, neglecting the Doppler shift and considering the polarizations, resonance can occur only near $z = -z'$ with $\sigma^+$ and near $z = z'$ with the $\sigma^-$ beam, so the atom is contained between $-z'$ and $z'$.

![Figure 4.9: 1-D MOT geometry](https://example.com/figure49.png)

Our initial trap design is shown in Figure 4.10. A pyrex cell was mounted inside super conducting magnetic gradient coils. The entire assembly was located in a double dewar (liquid nitrogen, liquid helium). Windows in the dewar and holes in the magnet allowed the laser light to reach the cell, as well as observation of fluorescent radiation with a cooled photomultiplier tube enhanced in the near infrared. The trap was operated as follows: a puff of helium gas, already cooled to 1.4 K, was introduced into the loading tube. A weak rf discharge was ignited at the bottom of the loading tube which extended a few millimeters beyond the orifice into the trap cell (about 1 atom in $10^6$ was excited to the metastable state). A fraction of the entering He($^2^3S$) atoms were
held in the MOT while the ground state atoms were pumped away by cold zeolite pellets that covered most of the cell bottom. A second zeolite cryopump attached to the loading tube above the discharge region ensured that the gas density in the loading tube dropped rapidly after the initial puff of gas was admitted. The discharge quenched when the gas density in the loading tube dropped below a few hundred millitorr. Most of the remaining gas was exhausted via the loading tube cryopump, minimizing the scattering of He(2³S) atoms.

\[\text{Figure 4.10: MOT apparatus. For clarity, the third axis laser beam, its mirror, and quarter-wave plate have not been shown.}\]

from the MOT by background gas entering through the orifice.

Trapping was not achieved with this design because the trap lifetime was limited by collisions with background gas. A new trap is under construction which should allow a near-perfect vacuum to be achieved in the trapping region. The lifetime of the trap will
then be limited to 10-100 msec by resonantly-enhanced He(2^3S) - He(2^3P) Penning reactions, however, techniques of chopping the laser beam should minimize this effect. Ultimately, it is estimated that using the present lasers a substantial number of atoms can be held at ultra-low temperature in a near-perfect vacuum for study.
Chapter Five

Conclusions

In operation, both lasers have demonstrated that they can provide efficient optical pumping of a collimated He(2³S) atom beam for periods of many hours resulting in stable beam polarizations approaching 100%. The output powers achieved represent the highest yield yet reported at this frequency for a single-mode laser. These powers are certainly sufficient for all experiments involving He(2³S) optical pumping currently envisioned. The specifications for the LNA laser are as follows:

- **Output Power** >300 mW with 5 W of 514 nm Ar⁺ pump
- **Output Beam Diameter** = 1.2 mm.
- **Output Beam Divergence (full angle)** = 1 mrad.

And for the CR899-21 Ti:Sapphire laser:

- **Output Power** = 300 mW with 21 W of all-lines Ar⁺ pump
- **Output Beam Diameter** = 1.0 mm.
- **Output Beam Divergence (full angle)** = 1 mrad.

Examination of the current LNA optical cavity and its behavior suggests that its performance and efficiency could be improved upon still further. The output power data suggest that even higher output powers might be realized with larger pump power, but this was not investigated because of the possibility of damage to the input faces of the LNA crystal. Use of a longer LNA crystal that absorbs a greater fraction of the pump power may also result in increased output powers, but problems associated with thermal lensing would be increased as well, and performance gains might be small. Curved cavity mirrors could be used to focus both the pump and the circulating laser power onto the crystal allowing the removal of the lenses from the cavity (though measurements have shown that the loss they represent is small), which might also lead to a higher output.
power. This would introduce astigmatism, however, and necessitate the use of a brewster-cut crystal (or compensating optic).

The CR899-21 Ti:Sapphire ring laser represents the vanguard of 1.083 μm Ti:Sapphire laser technology. Operation of the necessary large frame Argon laser has high annual maintenance costs. While tests of the ring LNA laser were undertaken using a large frame ion laser, the output power curve indicates that pumping with even a small frame Argon ion laser will result in output powers sufficient for the great majority of applications involving optical pumping and optical manipulation of He(2^3S) atoms.

Recent advances in diode lasers have lead to the production of InGaAs diodes capable of producing 1.083 μm radiation (J. S. Major and D. F. Welch, 1993). Distributed Bragg reflector (DBR) diode lasers are now sold commercially by Spectra Diode Laboratories that operate at 1.083 μm and produce 50 mW, though outputs as high as 200 mW have been reported (J. S. Major et al., 1994) with proper burn-in and operation. The output linewidth of the laser is ~ 30 MHz. Since the gain region is small, the beam divergence is large, but the beam can be collimated and shaped with lenses and apertures. None of these qualities really present insurmountable difficulties for helium optical pumping, except perhaps with regard to locking the laser frequency as rapid drifts of ~ 100 MHz. are common. For experiments requiring greater intensities, master oscillator - parametric amplifier (MOPA) diode lasers could be produced. Additionally, diode lasers are largely turn-key operation, and while the ring LNA was designed with ease of alignment in mind, it, and the Ti:Sapphire laser, are not.

Development of the 1.083 μm laser diodes provides stiff competition for argon ion pumped ring Ti:Sapphire and LNA lasers. However, another option that exists would be to pump the ring LNA laser with a high-brightness diode laser array which would reduce the operating costs significantly without, theoretically, sacrificing
performance. High-brightness diode arrays are available at 805 nm, at which (consulting Figure 3.1a) the LNA absorption spectrum shows a peak considerably higher than at 514 nm. This diode laser output, which could be collimated and apertured to approximate the TEM$_{0,0}$ mode, provides lower photon energies than the ion laser wavelength. Therefore, while the LNA should absorb a greater percentage of the pump light, it would not necessarily lead to increased thermal lensing of the crystal. Also, mounting of the diode array directly on the back end of the LNA ring laser chassis will reduce day-to-day beam walk which is the largest cause of laser misalignment and, with rigid optical mounts, would make the ring LNA laser system also largely turn-key. Thus a ring LNA laser may still be a good choice for many experiments involving He(2$^3$S).

The peak of the absorption curve for Ti:Sapphire occurs at about 500 nm. Unfortunately, no high-brightness diode array yet exists in this wavelength range and diode pumping of Ti:Sapphire is not yet feasible. In comparison to the ring LNA and 1.083 μm laser diodes, Ti:Sapphire does not appear to be the ideal choice for He(2$^3$S) studies. However, its broad tuning range gives it a big advantage in that it can be used not only to generate 1.083 μm radiation for He(2$^3$S) studies, but also radiation at other wavelengths for many other applications.
References


F. B. Dunning and P. Nordlander, *Nuclear Inst. and Meth. B*, in press.


Appendix A

The Planar-Mirror Fabry-Perot Etalon

The planar-mirror Fabry-Perot etalon (PFPS) (Figure A.1) can be formed in two ways. The first is a solid optical flat for which the two faces are highly parallel and coated identically. The second configuration consists of two solid optical flats, each of which is slightly wedged so that etaloning does not occur within the flats themselves. The two flats are arranged next to one another, with the inner faces parallel and coated identically, and the outer faces of the flats anti-reflection coated. While the transmission properties of the two configurations are the same, there are important differences with regard to their use as tuning elements within a laser cavity.

![Diagram A](image)

**(A)**

![Diagram B](image)

**(B)**

*Figure A.1: The possible PFPS configurations: (A) Single element (solid) and (B) two element (air-gap).*

To simplify somewhat the derivation (P. W. Milonni and J. H. Eberly, 1988) of the transmission properties of a PFPS (two component) it has been assumed that the anti-reflection coatings on the outer surfaces of the mirrors are perfect (in the case of the single element configuration, no corresponding surfaces exist to reflect - in all other ways both derivations are identical). This is certainly the case to the extent that contributions to the transmission by reflections occurring within the mirrors themselves will be negligible compared to the reflections occurring within the gap for sufficiently high
mirror reflectivities, and the wedge shape of the flats will reduce the significance of this effect still further. The angle of incidence of the beam upon the etalon (\(\Theta\)) must necessarily be small to prevent unacceptable walk-off losses, but for the time being it shall be included to be completely general.

Let each (identical) mirror be described by its complex reflection and transmission coefficients. \((r', t'\) for waves travelling into the gap, and \(r, t\) for waves travelling out). For monochromatic light of frequency \(f\), the phase shift introduced by a single propagation across the gap is given by:

\[
\Delta = \omega T
\]

Using \(\omega = 2\pi f\) and \(T = \text{ndcos}(\Theta)/c\) this becomes:

\[
\Delta = \frac{2\pi \text{ndcos}(\Theta)}{c}
\]

\[
\Delta = \frac{2\pi \text{ndcos}(\Theta)}{\lambda}
\]

Complex amplitudes for waves transmitted through the gap are then given by:

\[
t' A^{(i)}, t'(r')^2 A^{(i)} e^{2i\Delta}, t'(r')^4 A^{(i)} e^{4i\Delta}, ...
\]

(A-4)

Where \(A^{(i)}\) is the complex amplitude of the incoming wave.

If the first \(p\) transmitted waves are considered:

\[
A^{(i)}(p) = t' A^{(i)}[1 + (r')^2 e^{2i\Delta} + (r')^4 e^{4i\Delta} + ... + (r')^{2(p-1)} e^{2i(p-1)\Delta}]
\]

(A-5)

As \(p \rightarrow \infty\), this equation resembles the series

\[
1 + X + X^2 + X^3 + ... = 1/(1-X)
\]

with \(X = (r')^2 e^{2i\Delta}\).

Therefore,

\[
A^{(i)} = \frac{t' A^{(i)}}{1 - (r')^2 e^{2i\Delta}}
\]

(A-6)
From the Fresnel formulae it can be determined that:
\[
\begin{align*}
\tt' &= T \\
\tr &= r' \\
r^2 &= (r')^2 = R \\
R + T ( + A) &= 1
\end{align*}
\]

Where \( R \) and \( T \) are the usual reflection and transmission coefficients. \( A \) is the absorption or loss coefficient for the surfaces, which already has been assumed to be negligible. An \( A \) of \( < 0.50 \) is certainly within the available technology.

Substitution into A-6 above yields:
\[
A^{(0)} = \frac{TA^{(0)}}{1 - Re^{2i\Delta}} \tag{A-7}
\]

The corresponding transmitted intensity is given by
\[
I^{(0)} = A^{(0)}A^{(0)*}
\]

\[
I^{(0)} = \frac{T^2I^{(0)}}{(1-R)^2 + 4R\sin^2(\Delta)} \tag{A-8}
\]

\[
I^{(0)} = \frac{I^{(0)}}{1 + 4R\sin^2(\Delta)/(1-R)^2} \tag{A-9}
\]

Note that the transmission of this configuration will be 100\% for some wavelength regardless of the reflectivity of the optics (again, neglecting coating losses).

The Free Spectra Range (FSR) is defined as the frequency separation between adjacent maxima. Transmission maxima occurs for:
\[
\sin(\Delta) = 0
\]
\[
\Delta = k\pi \quad \text{for } k=0,1,2,\ldots
\]
\[
\text{FSR} = \frac{c}{2d(n)\cos(\Theta)} \tag{A-10}
\]

where \( n \) is the index of refraction of the material within the gap (\( n=1 \) for air).

The instrumental Finesse (\( F \)) is defined as:
\[ F = \frac{FSR}{FWHM} \]  

\[ I^{(0)}_{MAX} (\sin(\Delta) = 0) = 1 \]

So the following must be solved:

\[ \frac{1}{2} = \frac{1}{1 + 4R\sin^2(\Delta)/(1-R)^2} \]  

(\text{A-12})

\[ \sin^2(\Delta) = \frac{(1-R)^2}{4R} \]  

(\text{A-13})

\[ \sin(\Delta) = \pm \frac{(1-R)}{2(R)^{1/2}} \]  

(\text{A-14})

\[ \Delta = \sin^{-1} \left[ \frac{(1-R)}{2(R)^{1/2}} \right] = \frac{2\pi fd}{c} \]  

(\text{A-15})

\[ FWHM = \frac{c}{\pi d} \sin^{-1} \left[ \frac{(1-R)}{2(R)^{1/2}} \right] \]  

(\text{A-16})

And finally,

\[ F = \frac{\pi}{2} \{ \sin^{-1}[(1-R)/2(R)^{1/2}] \}^{-1} \]  

(\text{A-17})

This is known as the reflective finesse \( F_R \). There is another effect due to the flatness of the mirrors used in the construction of the etalon which is called the flatness finesse \( F_F \).

\[ F_F = M/2 \text{ for } \lambda/M \text{ mirrors} \]  

(\text{A-18})

This effect is due to the tendency of the mirror’s finite flatness to spread out otherwise sharp transmission peaks. Another effect which can limit the finesse of the device is caused by imperfect collimation of the incident light. This effect leads to what is known as the pinhole finesse \( F_P \).

\[ F_P = \frac{4\lambda L^2}{D^2 d} \]  

(\text{A-19})
Where \( L \) is focal length of the collimating lens, \( D \) is the diameter of the limiting aperture, and \( d \) is the distance between the mirrors. For applications involving laser sources the first two effects will represent the dominant contributions to the instrumental finesse \( (F_I) \).

\[
F_I^2 = F_R^2 + F_F^2
\]  

(A-20)

Tuning of a laser cavity using a single element PFPS is accomplished through rotation of the etalon about an axis parallel to the direction of laser polarization. Since this rotation adjusts the laser cavity round trip as well as the etalon passband, smooth tuning can be accomplished as long as the angular adjustment remains small. However, it is difficult to adjust the etalon in the precise, rigid manner necessary for good tuning and stability. For this reason, a PFPS utilizing two solid elements (also known as an air-gap etalon because of the space between the two elements) may have advantages. Tuning of the air-gap etalon is accomplished by adjusting the gap between the elements, often by mounting one or both of the elements on piezoelectric translators. This system allows for exact tuning with good stability. Adjustment of the gap, however, only tunes the etalon passband, but does not alter the laser cavity round trip. Therefore, it is necessary to use other elements, often a piezoelectrically-driven cavity mirror and a Brewster plate, to allow the laser cavity to “track” the etalon as it tunes. This may greatly complicate the electronics necessary for locking and tuning of the laser frequency.
Appendix B

ABCD Matrices and Cavity Stability

Calculations of the behavior of a laser beam as it travels through an optical system are necessary to the design of a laser cavity. While an exact solution of the problem would be quite difficult, two simplifying assumptions can be used which make the problem considerably easier:

1) The spread of the laser beam is negligibly small.

2) The spatial extent of the beam in the transverse direction is small in comparison to the size of the optical components which make up the cavity.

Using these two assumptions, the propagating laser beam can be treated as a ray, which marks the center of the path taken by this very small, slowly-diverging beam. In this sense then, simple geometric optics can be applied to solve the problem, but it is more convenient to develop a formalism to calculate the path the beam takes through the laser cavity and a means of calculating the stability of that cavity. This leads to the development of the ray matrix or ABCD matrix as it is called.

![Diagram of ray path](image)

**Figure B.1:** Propagation of a ray through a length d (Verdeyen, 1981).

In order to specify everything about the ray at any point within the cavity, it is only necessary to specify two things: Where is the ray with respect to an arbitrarily chosen axis? and In what direction is it heading? Application of trigonometry to Figure

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B.1, along with the assumption that the angle between the axis and the ray is necessarily small (namely \( \sin \theta = \tan \theta \approx \theta \)), leads to:

\[
\begin{align*}
    r_2 &= r_1 + d \cdot r'_1 \\
    r'_2 &= r_1 + 1 \cdot r'_1
\end{align*}
\]  

(B-1)  

(B-2)

Where \( r'_{1,2} \) is the slope of ray \( r_{1,2} \). These can be rewritten in matrix form as:

\[
\begin{bmatrix}
    r_2 \\
    r'_2
\end{bmatrix} = \begin{bmatrix}
    1 & d \\
    0 & 1
\end{bmatrix} \begin{bmatrix}
    r_1 \\
    r'_1
\end{bmatrix}
\]

(B-3)

In general, the relationship between the input and output rays of an optical system is given by an ABCD matrix:

\[
\begin{bmatrix}
    r_{\text{OUT}} \\
    r'_{\text{OUT}}
\end{bmatrix} = \begin{bmatrix}
    A & B \\
    C & D
\end{bmatrix} \begin{bmatrix}
    r_{\text{IN}} \\
    r'_{\text{IN}}
\end{bmatrix}
\]

(B-4)

These matrices can be derived for a number of optical components. It is important to note that the determinant of this matrix is always unity (provided the index of refraction is the same on the input and exit planes), that is:

\[
AD - BC = 1
\]

(B-5)

When the matrices are applied to a system of components which make up a laser resonator, they can be used to determine the \textit{stability} of the cavity. That is, a ray within the cavity, after many round trips, remains within the cavity and does not "walk off" one of the optical components.

Consider a ray making its \( n \)th pass through a resonator. Then from B-4:

\[
\begin{align*}
    r_{n+1} &= A \cdot r_n + B \cdot r'_{n} \\
    r'_{n+1} &= C \cdot r_n + D \cdot r'_{n}
\end{align*}
\]

(B-5)  

(B-6)

Equation B-5 can be rewritten to read:

\[
    r'_n = \frac{1}{B} (r_{n+1} - Ar_n)
\]

(B-7)
Adjustment of the indices of B-7 to represent the \((n+1)^{st}\) round trip allows it to be equated with B-6 so:

\[
\begin{align*}
    r'_{n+1} &= \frac{1}{B} \left( r_{n+2} - Ar_{n+1} \right) = C \cdot r_n + D \cdot r'_n = Cr_n + \frac{D}{B} (r_{n+1} - Ar_n) \\
    r_{n+2} - Ar_{n+1} &= BCr_n + Dr_{n+1} - ADr_n = Dr_{n+1} - (AD - BC)r_n = Dr_{n+1} - r_n \\
    r_{n+2} - 2 \left( \frac{A+D}{2} \right) r_{n+1} + r_n &= 0
\end{align*}
\]

(B-8)

The solutions to this equation which are useful are those which are bounded. Solutions for which \(r\) has some maximum value will remain within the resonator; solutions for which \(r\) is unbounded will eventually "walk off" one of the resonator components. In searching for a solution to B-8, then, a good guess would be a trigonometric function of the form:

\[
r_n = r_0 e^{i\theta}
\]

Substitution into B-8 yields:

\[
r_0 e^{i\theta} \left[ e^{2i\theta} - 2 \left( \frac{A+D}{2} \right) e^{i\theta} + 1 \right] = 0
\]

(B-9)

Certainly the case for which \(r_n = r_0 e^{i\theta} = 0\) is of little interest because the ray simply bounces back and forth along the axis. To be completely general in solution, the bracketed term in B-9 must be zero. This is an equation which is quadratic in \(e^{i\theta}\) which has solutions:

\[
e^{i\theta} = \frac{A+D}{2} \pm j \left[ 1 - \left( \frac{A+D}{2} \right)^2 \right]^{1/2}
\]

(B-10)

If all the quantities in B-10 are real, then the solutions to B-8 are linear combinations of the form:

\[
r_n = r_0 e^{i\theta} + r_0^* e^{-i\theta}
\]

or

\[
r_n = r_{\text{MAX}} \sin(n\theta + \alpha)
\]

(B-11)
Note that if the quantities in B-10 were not real, then B-11 would have to be rewritten because \( r \), the position of the beam within the resonator, must be real. Given this criteria, then, the solutions of B-10 are restricted, namely:

\[
1 - \left( \frac{A+D}{2} \right)^2 \geq 0
\]

or

\[
0 \leq \frac{A+D+2}{4} \leq 1
\]

(B-12)

Solutions which fulfill this requirement are stable with bounded values of \( r \). Solutions outside of this region are considered \textit{unstable}. Solutions on the border are called \textit{conditionally stable}.

Consider then the application of ABCD matrices to the cavity design of the ring LNA laser shown in Figure B.2.

![Diagram of the ring LNA laser](image)

\textbf{Figure B.2:} Physical layout of the ring LNA laser. Both lenses have matched focal length \( f \). Both are a distance \( d \) from the crystal. For simplicity, the crystal-lens system is centered in the 1-4 arm (i.e. \( d_{14} = 2d + 2d_1 \)), but this is not necessarily the case, nor would it change the ray matrix calculation significantly if it were otherwise. All mirrors are flat.

An additional ABCD matrix which will be required is that for the propagation through a thin lens of focal length \( f \):

\[
\begin{bmatrix}
1 & 0 \\
-\frac{1}{f} & 1
\end{bmatrix}
\]
The ABCD transmission matrix for this system of components then becomes:

\[
\begin{bmatrix}
1 & d_1 \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & 0 \\
\frac{1}{f} & 1
\end{bmatrix}
\begin{bmatrix}
1 & 2d \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & 0 \\
\frac{1}{f} & 1
\end{bmatrix}
\begin{bmatrix}
1 & d_{34} \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & d_{23} \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & d_{12} \\
0 & 1
\end{bmatrix}
\]

The action of the crystal in the cavity can be neglected because it acts, at worst, as a crystal of very long focal length. This set of matrices can be multiplied out to get the stability criteria for this cavity.

\[
0 \leq \frac{A + D + 2}{4} = 1 + \frac{d}{2f^2(D-2d)} - \frac{D}{2f} \leq 1
\]

Which can be rewritten to give:

\[
\frac{2(d^2-f^2)}{(d-f)} \leq D \leq \frac{2d^2}{(d-f)} \tag{B-12}
\]

Where \(D = d_{12} + d_{23} + d_{34} + d_{41}\) is the round trip distance.

The focal length of the lenses, 7.6 cm (3 inches), has been found experimentally to provide maximum output power with minimum danger of damage to one of the crystal faces due to the focused pump beam. The distance from the crystal to the lens which provides maximum output power has also been found experimentally to be approximately 7.9 cm (3.125 inches). Inserting these values into B-12 gives the restriction on the entire cavity round trip to be:

\[
31 \text{ cm} \leq D \leq 397 \text{ cm}
\]

This does not seem to give a lot of information about the laser cavity construction given that the range covers over an order of magnitude, but this information is the first step in laser cavity design which answers the vital question "Will the system lase at all?" Other considerations will need to be addressed to determine if there are further restrictions upon the round trip distance, or if the round trip is arbitrary within these limitations.
Appendix C
Gaussian Beams

While the optical ray is useful for calculations under many circumstances, such as cavity stability criteria (see Appendix B), it must be remembered that it has limited physical reality. It does not carry with it the information of a real optical beam. It does not have an amplitude, phase, or spatial extent. It is for this reason that a more realistic picture of the beam traveling within the laser cavity must be developed (Verdeyen, 1981).

A good starting point is the realization that an optical beam propagating within a laser resonator behaves mostly like a TEM (transverse electric and magnetic) travelling wave in that the field components lie in a plane perpendicular to the direction of propagation. This leads to an application of the (time independent) wave equation:

\[ \nabla^2 E + \frac{\omega^2}{c^2} n^2 E = 0 \]  \hspace{2cm} (C-1)

This can be broken up into the longitudinal and transverse directions (allowing the z axis to be the direction of propagation):

\[ \nabla_z^2 E + \frac{\partial^2 E}{\partial z^2} + \frac{\omega^2}{c^2} n^2 E = 0 \]  \hspace{2cm} (C-2)

The solution to C-2 should have an amplitude, and spatial extent, and should propagate something like a plane wave, in order to describe the circulating laser beam. A good guess, then, would look like:

\[ E(x,y,z) = E_0 \psi(x,y,z) e^{-jkz} \]  \hspace{2cm} (C-3)

Where \( k = 2\pi n / \lambda = \omega n / c \) is the wavenumber, and \( E_0 \) is the amplitude. Substitution yields:

\[ \nabla_z^2 \psi + \frac{\partial^2 \psi}{\partial z^2} + j2k \frac{\partial \psi}{\partial z} = 0 \]  \hspace{2cm} (C-4)

For typical optical frequencies, \( k \) is going to be a very large number, while it is assumed that the variation of \( \psi \) and \( \partial \psi / \partial z \) along distances on the order of a wavelength will be
small. Therefore, the second term in C-4 is neglected in comparison to the third. This leads to the central equation for Gaussian Beams which is often called the paraxial wave equation:

\[ \nabla^2 \psi - j2k \frac{\partial \psi}{\partial z} = 0 \]  
(C-5)

The lowest order mode for a laser is the TEM\(_{0,0}\) mode. It is a single spot with cylindrical symmetry. With these considerations, C-5 becomes:

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) - j2k \frac{\partial \psi}{\partial z} = 0 \]  
(C-6)

It is "guessed" that the solution of C-6 is of the form:

\[ \psi_0 = \exp \left\{ -j \left[ P(z) + \frac{kr^2}{2q(z)} \right] \right\} \]  
(C-7)

Where the subscript 0 indicates that this is the lowest order mode. Substitution into C-6 allows for solution (an interpretation) of the quantities \( P(z) \) and \( q(z) \).

\[ \left\{ \left[ \frac{k^2}{q^2(z)} \left( q'(z) - 1 \right) \right] r^2 - 2k \left[ P'(z) + \frac{j}{q(z)} \right] \right\} \psi_0 = 0 \]  
(C-8)

For the form C-7 to be a solution, the bracketed terms in C-8 must be zero.

\[ q'(z) = 1 \]  
(C-9a)

\[ P'(z) = -\frac{j}{q(z)} \]  
(C-9b)

In general \( q(z) \) will be complex:

\[ q(z) = z + jz_0 \]  
(C-10)

If the \( z=0 \) axis of the wave is considered (without, at this time, stating where \( z=0 \) is):

\[ q(z=0) = jz_0 \]

\[ \psi_0(z=0) = \exp \left( -\frac{kr^2}{2z_0} \right) \exp \left[ -jP(z=0) \right] \]
The first exponential term indicates that the amplitude of the wave drops off rapidly in the transverse direction with increasing $r$. This allows for the definition of a scale length for the beam.

$$\omega_0^2 = \frac{2\lambda z_0}{k} = \frac{\lambda z_0}{\pi}$$  \hspace{1cm} (C-11)

In the transverse direction, the laser beam appears as a circle, with most of the power contained within a radius $\sim \omega_0$, and for this reason $\omega_0$ is often known as the spot size.

To find the behavior of the beam at any point $z$, return to the original solution for $q(z)$ given by C-10:

$$\frac{1}{q(z)} = \frac{1}{z + jz_0} = \frac{z}{z^2 + z_0^2} \cdot \frac{z_0}{z^2 + z_0^2}$$  \hspace{1cm} (C-12)

$$\psi_0 = \left\{ \exp\left[-\frac{kz_0r^2}{2(z^2 + z_0^2)}\right] \right\} \left\{ \exp\left[-\frac{jkr^2}{2(z^2 + z_0^2)}\right] \right\} \{\exp[-jP(z)]\}$$  \hspace{1cm} (C-13)

Again, the first bracketed term indicates a scale length of the beam in the transverse direction.

$$\omega^2(z) = \frac{2}{kz_0} (z^2 + z_0^2) = \frac{2z_0}{k} \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]$$

Which can be rewritten using the definition given by C-11.

$$\omega^2(z) = \omega_0^2 \left[ 1 + \left( \frac{\lambda z}{\pi \omega_0} \right)^2 \right]$$  \hspace{1cm} (C-14)

At $z = 0$ the beam spot size is at a minimum. From there the gaussian beam diverges outward in the transverse direction. At large distances ($z \gg z_0$), the beam waist increases linearly:

$$\omega(z \gg z_0) = \omega_0 \frac{z}{z_0} = \frac{\lambda z}{\pi \omega_0}$$

The divergence (half) angle of the beam then asymptotically approaches:
\[ \frac{\theta}{2} = \frac{d\omega}{dz} = \frac{\lambda}{2\pi \omega_0} \]

The physical interpretation of the second term in C-13 is clearer if the following definition is made:

\[ R(z) = \frac{1}{z} \left[ z^2 + z_0^2 \right] = z \left[ 1 + \left( \frac{z_0}{z} \right)^2 \right] \]

\[ R(z) = z \left[ 1 + \left( \frac{\pi \omega_0^2}{\lambda z} \right)^2 \right] \quad (C-15) \]

Then C-13 becomes:

\[ \psi_0 = \left\{ \exp \left[ -\frac{r^2}{\omega_0^2(z)} \right] \right\} \left\{ \exp \left[ -\frac{jkz^2}{2R(z)} \right] \right\} \{ \exp[-jP(z)] \} \quad (C-16) \]

The second term now looks like a phase factor which indicates that the plane \( z = 0 \) is not an equiphasic surface. The local field lags (for positive \( R(z) \)) behind that at \( r = 0 \) for increasing \( r \). So what is the shape of the wavefront? Consider the field for a wave expanding from a point source propagating in the \( z \) direction.

\[ E \sim \frac{1}{R} \exp(-jkR) \quad (C-17) \]

where \( R = (r^2 + z^2)^{1/2} \). For large distances, \( R \sim z \gg r \), the binomial theorem can be used as follows:

\[ R = z \left( 1 + \frac{r^2}{z^2} \right)^{1/2} \sim z + \frac{1}{2} \frac{r^2}{z} \sim z + \frac{1}{2} \frac{r^2}{R} \]

So C-17 can be rewritten:

\[ E \sim \frac{1}{R} \exp(-jkz) \exp \left( -\frac{jkz^2}{2R} \right) \]

The last term looks like the second term in C-16, and hence is called the radial phase factor. For a gaussian beam, the center of curvature changes as given by C-15. As \( z \to 0 \), the center of curvature moves back, until at \( z = 0 \) (recall, where the beam waist is also a minimum), the center is at infinity, and the wavefront is planar.
Next, $P(z)$ can be calculated from C-9b:

$$P'(z) = \frac{-j}{q(z)} = \frac{-j}{z + jz_0}$$

$$jP(z) = \ln \left[ 1 - j \frac{z}{z_0} \right] = \ln \left\{ \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]^{1/2} \exp \left[ -j \tan^{-1} \left( \frac{z}{z_0} \right) \right] \right\}$$

$$\exp[-jP(z)] = \frac{1}{[1 + (z/z_0)^2]^{1/2}} \exp[j\tan(z/z_0)] = \frac{\omega_0}{\omega(z)} \exp[j\tan^{-1}(z/z_0)]$$

And C-16 can be rewritten:

$$\psi_0 = \frac{\omega_0}{\omega(z)} \left\{ \exp \left[ -\frac{r^2}{\omega^2(z)} \right] \right\} \left\{ \exp \left[ -\frac{jkr^2}{2R(z)} \right] \right\} \left\{ \exp \left[ j\tan^{-1} \left( \frac{z}{z_0} \right) \right] \right\}$$

The first term represents an adjustment to the amplitude of the wave in the propagation direction. The last term is called the longitudinal phase factor, and expresses the change in phase of the wave in the propagation direction.

So, to summarize the results for the TEM$_{0,0}$ beam (Verdeyen, 1981):

$$\frac{E(x,y,z)}{E_0} = \left\{ \frac{\omega_0}{\omega(z)} \exp \left[ -\frac{r^2}{\omega^2(z)} \right] \right\} \times \exp \left\{ -j \left[ k \left( \frac{z}{z_0} \right) \right] \right\} \times \exp \left[ -\frac{jkr^2}{2R(z)} \right]$$

amplitude factor

longitudinal phase

radial phase

where

$$\omega^2(z) = \omega_0^2 \left[ 1 + \left( \frac{\lambda z}{\pi \omega_0^2} \right)^2 \right] = \frac{2z_0}{k} \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]$$

$$R(z) = z \left[ 1 + \left( \frac{\pi \omega_0^2}{\lambda z} \right)^2 \right] = z \left[ 1 + \left( \frac{z_0}{z} \right)^2 \right]$$

$$z_0 = \frac{\pi \omega_0}{\lambda}$$

The equation for higher order TEM$_{m,n}$ modes is as follows and can be verified by direct substitution into C-5:
\[
\frac{E(x,y,z)}{E_{mn}} = \left\{ \frac{\omega_0}{\omega(z)} \exp\left[ -\frac{x^2 + y^2}{\omega_0^2(z)} \right] \right\} H_m \left[ \frac{x \sqrt{2}}{\omega(z)} \right] H_n \left[ \frac{y \sqrt{2}}{\omega(z)} \right] \\
\times \exp \left\{ -j \left[ k z - (1 + m + n) \tan^{-1} \left( \frac{z}{z_0} \right) \right] \right\} \\
\times \exp \left[ -\frac{jkr^2}{2R(z)} \right]
\]

Where \( H_n(u) \) is the Hermite polynomial of order \( n \) with argument \( u \), and all other symbols are as defined previously. In many cases, a laser will naturally select the TEM\(_{0,0}\) mode as it matches (presumably) the mode of the pump laser. However, if a laser is lasing preferentially on some other TEM mode, the lowest order mode can be forced simply by installing an aperture of the proper diameter into the cavity.

The TEM\(_{0,0}\) mode is preferred because it is the mode with the highest power density. Additionally, when sent through a series of optics, it collimates with smooth beam waists with minimal beam distortion. Higher order modes are difficult to transmit and focus, and their uneven spatial illumination can make experimentation impossible.

Continuing, then, with the design of a laser resonator, it would be extremely useful if some connection could be drawn between the ABCD matrices (Appendix C), with which the cavity stability criteria were developed, and the gaussian beam mathematics here. Though difficult to prove in general, such a connection exists and it is given as follows:

\[
q_2 = \frac{Aq_1 + B}{C q_1 + D} \quad (C-18)
\]

\( q_2 \), the complex beam parameter at the exit plane, is related to \( q_1 \), the complex beam parameter at the entrance plane, through the ABCD transmission matrix for the optical elements between the two planes.

This can be applied to a laser cavity by forcing the complex beam parameter to equal itself after a round trip through the cavity:

\[
q(z_1 + \text{round trip}) = q(z_1)
\]
Or, by application of C-18:

\[ q(z_1) = \frac{Aq(z_1) + B}{Cq(z_1) + D} \] (C-19)

Which is an equation quadratic in \( q(z_1) \) with solution:

\[ \frac{1}{q(z_1)} = -\frac{A - D}{2B} \pm \frac{1}{B} \left[ \left( \frac{A - D}{2} \right)^2 + BC \right]^{1/2} \]

Recalling that \( AD - BC = 1 \), this can be rearranged to look like C-12:

\[ \frac{1}{q(z_1)} = -\frac{A - D}{2B} - j \frac{B}{2} \left[ 1 - \left( \frac{A + D}{2} \right)^2 \right]^{1/2} \]

From this, the radius of curvature of the beam and the beam waist size can be found by comparison with C-14,15 to be:

\[ R(z_1) = -\frac{2B}{A - D} \]

\[ \frac{\pi \omega^2(z_1)}{\lambda} = \left[ \frac{B}{1 - \left( \frac{A + D}{2} \right)^2} \right]^{1/2} \] (C-20)

These beam parameters are for any plane \( z_1 \) where the round trip starts (and stops). It can be applied to any laser cavity to find the beam parameters at any point.

Furthermore, C-18 can be used to find how a gaussian beam is focused. This is important in the design of the LNA laser because the 514 nm beam of the Argon ion laser is focused onto the crystal forming a beam waist. It is this waist that the beam in the cavity must overlap if the laser is to have maximum pump conversion efficiency.

Calculation of the gaussian beam focus starts with the ABCD matrix for a lens plus a length of free space \( z \):

\[ T = \begin{bmatrix} 1 - \frac{z}{f} & z \\ -\frac{1}{f} & 1 \end{bmatrix} \]

With the application of C-18 and some algebra, it can be shown that:
\[
\frac{1}{R(z)} = \frac{-1/f + z(1/f^2 + 1/z_0^2)}{(1 - z/f)^2 + (z/z_0)^2}
\]  
(C-21)

\[
\frac{\lambda}{\pi \omega_0^2(z)} = \frac{1/z_0}{(1 - z/f)^2 + (z/z_0)^2}
\]  
(C-22)

where \( z_0 = \pi \omega_0^2/\lambda \).

By minimizing C-22, it is found that the beam waist is at its smallest, not at the focus of the lens as would be expected, but rather at:

\[
z_M = \frac{f}{1 + (f/z_0)^2}
\]

However, under normal conditions \( \lambda \ll \omega_0 \), therefore \( z_0 \gg f \) and \( z_M \sim f \). From this the focused beam waist can be predicted to be:

\[
\frac{\lambda}{\pi \omega_M^2(z)} = \frac{1/z_0}{(1 - z_M/f)^2 + (z_M/z_0)^2}
\]

\[
\omega_M \approx \frac{\lambda f}{\pi \omega_0}
\]

(C-23)

Application to the design of the LNA laser is as follows:

The Argon ion beam is, allowing for aging and changes in the tube windows and optics, approximately 1.5 mm in diameter (\( \omega_0 = .75 \) mm). The wavelength is 514.5 nm. The focal length of the lens is 7.5 cm. Then, \( z_0 = 13.7 \) m >> f. The approximation made (C-23) above is certainly valid, and the beam waist of the focused Argon ion beam is \( \omega_M = 16.6 \mu \text{m} \). Application of C-19, 20 to the matrices of the LNA laser (Appendix B) using the crystal center as the start/end point of the round trip leads to:

\[
\frac{\sqrt{d - f} \sqrt{2d^2 - (d - f)D}}{\sqrt{D - 2(d + f)}} = \frac{\pi \omega^2}{\lambda}
\]

(C-24)

Where D is the round trip distance, f is the focal length of the lenses, and d is the distance between the lenses and the crystal. Using the same numbers found experimentally as in Appendix B (\( f = 7.6 \) cm [3 inches], \( d = 7.9 \) cm [3.125 inches]), Figure C.1 is generated.
The first conclusion that can be drawn from looking at C-24 is that, because the beam waist must necessarily be real, that D is limited to the range $31 \text{ cm} \leq D \leq 397 \text{ cm}$. This is the same as the result obtained in Appendix B. The second result of C-24 is that the beam waist within the crystal is fairly insensitive to the round trip distance for this cavity arrangement. Over a broad range the beam waist is roughly 30 $\mu$m, which is sufficient to overlap the Argon ion pump beam waist. A round trip distance of approximately 2 m is chosen then because it lies in the center of the shoulder, allowing small variations in the laser cavity alignment to leave the rest of the cavity unaffected.

This analysis can be reversed to study the tolerance in the position of the lenses with respect to the crystal. By fixing the round trip cavity distance at 2m, and using the lens focal length of 7.6 cm, the variation of the beam waist at the crystal with the position of the lenses can be calculated using C-24 and is shown in Figure C.2.

The final concern that must be addressed with regard to the overall cavity design is that of beam divergence. As the beam propagates around the cavity it will diverge, and
it may diverge to the point that it will not pass through optics used within the cavity without clipping. In this laser, the smallest aperture in use is that of the optical diode. TGG, of which the optical diode is constructed (see Chapter 3), is extremely expensive, so the diameter of the piece used is small. The diameter of the optical diode is about 1 cm, but the diameter of the usable region is probably slightly smaller than that. The calculation which lead to C-24 can be repeated using the output coupler as the start/end of the round trip to find the beam diameter at that point. The result is not nearly as compact because the cavity lacks the symmetry about the output coupler that is evident from the standpoint of the crystal. The calculation indicates a beam waist of about 0.6 mm. at the output coupler, which will easily pass unclipped through any component in use, even allowing for misalignment. The resulting divergence (half) angle ~0.5 mrad.
Appendix D

Laser Linewidth Calculation

The calculation of the laser linewidth is important in many atomic studies because a laser, while possessing a narrow linewidth, does not possess an infinitely narrow one. When pumping atomic transitions, the concern is that the laser linewidth be such that it is possible to excite a single transition, even in the presence of neighboring transitions. The following derivation will allow an upper limit to the laser linewidth to be calculated.

The ratio of the operating frequency of a laser cavity to its output linewidth is known as the quality factor, or $Q$, of the cavity.

$$Q = \frac{v_0}{\Delta v_{1/2}} \quad (D-1)$$

Another means of calculating the $Q$ of a cavity is through the energy loss per round trip (Verdeyen, 1981):

$$Q = \omega_0 \left( \frac{\text{energy stored in the system at resonance}}{\text{average power lost per round trip}} \right) \quad (D-2)$$

Where $\omega_0$ is the angular frequency of the cavity. If the input power to the laser cavity is removed, then the power in the cavity will decrease with time and $D-2$ can be rewritten:

$$Q = \omega_0 \frac{W}{dW/dt}$$

Where $W$ is the energy stored in the system at any time $t$. The $Q$ calculated in this way is often called the "bare cavity" or "cold cavity" $Q$. It neglects the stimulated emission contribution to the laser output, and as such will arrive at a value of $Q$ which is significantly lower than the actual $Q$ of the cavity. This equation has solution:

$$W(t) = W_0 \exp \left( -\frac{\omega_0}{Q} t \right) \quad (D-3)$$

The energy stored in the cavity at any time can also be calculated by photon counting and using the inherent losses of the cavity. Consider a laser cavity of round trip distance $D$
with round trip loss percentage \( L \). If the laser is operated and then the input power removed, the population of the photons \( \phi_p \) would decrease:

\[
\frac{d\phi_p}{dt} = - \left( \frac{L}{D/c} \right) \phi_p
\]

Where \( D/c \) is the round trip time. (This also neglects photons produced via stimulated emission.) This equation has solution:

\[
\phi_p(t) = \phi_{p0} \exp \left( -\frac{t}{\tau_p} \right)
\]

(D-4)

where \( \tau_p \) is the photon lifetime within the cavity. But the photon count in the cavity times the energy per photon is the energy in the cavity, so it is possible to compare D-3 and D-4 to find:

\[
\tau_p = \frac{Q}{\omega_0}
\]

Or, using D-1,5 gives:

\[
\Delta v_{1/2} = \frac{L}{2\pi(D/c)}
\]

It must again be stressed that the linewidth calculated in this fashion is an upper limit. This calculation ignores stimulated emission effects upon which laser physics is founded. That is not to say that it is without merit. It allows an order of magnitude estimate of the linewidth without knowing the single pass gain of the medium, the atom level structure of the medium, and other quantities which are necessary to an exact calculation.

This approximation leaves only the difficulty of accurately calculating the round trip losses for the cavity in question. For the ring LNA, the output coupler is 95% reflective. From there, and upper bound can be placed on the losses by simply assuming
a 1/2% loss for every surface the beam hits during the round trip (in most cases this should be adequate because mirrors with 99.5% reflectivities are common, as are anti-reflection coatings of better than 1/4%). This approximation leads to round trip losses of ~15%, which gives a linewidth of:

$$\Delta v_{1/2} = \frac{7.2}{D(\text{meters})} \text{ MHz.}$$

There has been no special attempt made to isolate the ring LNA laser from mechanical vibration of the resonator so a few MHz of jitter is to be expected. Therefore, this linewidth should accurately reflect the effective linewidth of the laser. Additionally, the closest pair of Helium transitions \((D_1-D_2)\) is 2.3 GHz, so there is no need to pay special attention to further narrowing the laser linewidth. A round trip distance of two meters will result in a reasonable upper limit to the linewidth (3.6 MHz.) while leaving adequate space for all optical components.
Appendix E

Collected Publications

On the following pages are the collected copies of publications from this laboratory which are related to the present work.
Dynamics of Penning ionization reactions involving He(2 $^3S$) metastable atoms


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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 between He(2 $^3S$) atoms and H$_2$O, SO$_2$, NO, and NO$_2$. The data complement earlier studies of the reaction dynamics based on analysis of the energy distribution of the product electrons and confirm that ionization can occur via a number of different reaction channels. For example, the present results show that in collisions with target gases having a positive electron affinity, ionization via the ionic channel is important and that effects due to spin-orbit coupling must be considered. The data also provide evidence that exchange may be important in collisions with open-shell targets.

Recent work in this laboratory has shown that the dynamics of Penning ionization (PI) reactions of the type

$$\text{He}(2^3S) + \text{X}^\cdot \rightarrow \text{He}(1^3S) + \text{X}^\cdot + e^-.$$   \hspace{1cm} (1)

that involve He(2 $^3S$) metastable atoms and a variety of molecular targets XY can be examined by means of spin labeling techniques that involve the use of electron-spin-polarized He(2 $^3S$) atoms coupled with energy-resolved measurements of the spin of the product electrons. This approach complements earlier studies of PI reaction dynamics that were based on analysis of the energy distribution of the product electrons. Data obtained using H$_2$O, SO$_2$, NO, and NO$_2$ target gases are presented that reveal a number of different reaction channels and show that, under certain conditions, exchange and spin-orbit effects can be important.

The present apparatus is shown schematically in Fig. 1 and has been described in detail elsewhere. Briefly, He(2 $^3S$) atoms are created in a flowing helium afterglow and are polarized by optical pumping. Target gas is then introduced into the afterglow, resulting in the production of Penning electrons, a fraction of which escape from the afterglow through a differentially pumped aperture. The electron polarization is measured, as a function of energy, using a hemispherical energy analyzer in series with a Mott polarimeter.

The helium afterglow is contained in a 10-cm-diam Pyrex flow tube that is exhausted by a high-speed Roots pump. To minimize stray electric fields, the tube is lined with copper sheet. Helium gas entering the flow tube passes through a constricted region where it is excited by a microwave discharge which creates predominantly 2 $^3S$, rather than 2 $^3P$, metastable atoms. 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-extractor separation (80 cm), (unpolarized) source-produced electrons can, under certain conditions, provide a small contribution to the extracted electron current at energies $\leq$ 1 eV and data are therefore not reported in this energy regime.

A weak magnetic field ($\sim 0.2$ G) is applied perpendicular to the axis of the flow tube to establish a well-defined quantization axis. Circularly polarized 1.08 $\mu$m 2 $^3S_1\rightarrow$ 2 $^1P_1$ radiation from a single-mode, frequency-stabilized lanthanum neodymium magnesium hexaluminate (LNA) laser is incident along the magnetic field direction and is used to optically pump the 2 $^3S$ atoms to increase the relative population in the $M_f(M_s) = +1$ (or $-1$) magnetic sublevel. Target gas is injected into the flow tube close to the extraction aperture using a fine hypodermic needle. Electrons produced in PI reactions diffuse to the walls of the flow tube under essentially field-free conditions without significant energy loss and those that pass through the extraction aperture are formed into a beam by a series of electrostatic lenses. The extracted electrons are energy analyzed using a hemispherical energy analyzer (which has an energy resolution of $\sim 0.4$ eV) and their polarization is measured using a compact retarding-potential Mott polarimeter. Tests showed that, without the exception of NO, the measured electron distributions (EEDs) and polarizations were insensitive to target-gas flow rate over a wide range. For NO, exchange in $e^-$/NO collisions was observed to lead to significant degradation in electron polarization at high flow rates and data were therefore only recorded at low NO flow rates.

Prior to each experimental run, the polarization $P_1$ of the 2 $^3S$ atoms was determined by admitting Ar to the flow tube and measuring the polarization of the extracted electrons. Previous work in this laboratory has demonstrated that spin is conserved in PI reactions with Ar and that the polarization of the product electrons is equal to that of the 2 $^3S$ atoms. The 2 $^3S$ polarization was typically $\sim 0.7$ 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 and their polarization is quite large, typically $\sim 70\%$ that of the 2 $^3S$ atoms. This spurious electron signal is substantially reduced, however, upon admix-
section of target gas because the majority of $^2 \Sigma^+$ atoms are deexcited in gas-phase collisions. Thus contributions from surface ejection are unimportant except in energy regimes where the Penning electron signal is small.

Electron energy distributions measured following PI reactions with H$_2$O, SO$_2$, NO, and NO$_2$ are shown in Figs. 2(a)–2(d), respectively, together with the corresponding energy-resolved electron polarizations, which are expressed as a percentage of the initial $^2 \Sigma^+$ polarization. Figure 2 also includes EED's measured (with higher energy resolution) by earlier workers using beam and gas cell techniques. The general characteristics of the earlier data are reproduced 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 the higher electron energies.

Earlier analyses of Penning electron energy distributions using a potential-curve model have shown that in many cases PI can be described in terms of a direct transition from the covalent He($^2 \Sigma^+$)+XY entrance potential to the final He($^1 \Sigma^+$)+XY$^+$ exit potential. Because neither potential is strongly dependent on internuclear separation, ionization via this "covalent" channel typically results in a narrow distribution of Penning electron energies. For targets with a positive electron affinity, however, ionization may be preceded by a transition from the covalent entrance potential onto a strongly attractive He$^+$+XY$^-$ ionic potential. Since this potential changes rapidly with internuclear separation, ionization via this "ionic" channel leads to a broad distribution of electron energies. The He$^+$−XY$^-$ collision complex may also decay through transitions to a He($^1 \Sigma^+$)+XY$^{**}$ exit potential and the XY$^{**}$ molecular Rydberg states so formed may, in turn, dissociate yielding ground- and excited-state atoms. Autodissociation of such excited atoms, and of the XY$^{**}$ molecular Rydberg states, can give rise to additional features in the electron energy distribution.

The EED observed with H$_2$O comprises three peaks associated with production of H$_2$O$^+$ ions in the ground $^2 \Sigma^+$ and $^4 \Pi$, and excited $^4 \Pi(3\nu_2)$, and $^2 \Sigma^+$($1\nu_2$) states. (The H$_2$O anion from which the electron is removed is indicated in the brackets.) Ionization occurs via covalent channels, the widths of the various peaks resulting from population of different product ion vibrational states. The electron polarization associated with the $^2 \Sigma^+$ and $^4 \Pi$ features is large and, to within experimental error, is equal to that of the $^2 \Sigma^+$ atoms indicating that spin is conserved. [The error bars represent only statistical uncertainties and do not include possible systematic errors associated with measurement of the He($^2 \Sigma^+$) polarization or contributions from surface ejection.] The measured polarizations decrease somewhat at lower energies but this may result from instrumental effects. Difficulties were experienced in ob-
taining reproducible data for $H_2O$ at the lowest energies, possibly a consequence of surface charging due to condensation on surfaces in the vicinity of the extractor. Recent studies involving surface Penning ionization from several monolayer-thick films of $H_2O$ molecules condensed on a cooled surface revealed no decrease in electron polarization at the lower energies.\textsuperscript{10} The available data suggest, therefore, that spin is conserved in PI reactions with $H_2O$ which must proceed through the covalent channel via Auger-type processes in which an electron of appropriate spin from the target molecule tunnels into the $1s$ core hole in the $2S$ atom with simultaneous ejection of the (polarized) $2p$ electron, i.e., via the reaction

$$\text{He}(2S)\left< 1s \right> + H_2O\left< 1s \right> \rightarrow \text{He}(1S)\left< 1s \right> + H_2O^+\left< 1s \right> + e^-\left< 1s \right> \quad (2)$$

This is consistent with the model for PI adopted by Haug et al.\textsuperscript{11} in interpreting the EED in which the ionization probability is assumed to be proportional to the overlap between the $H_2O$ molecular orbital from which the electron is removed and the $2S\left< 1s \right>$ core hole. Interestingly, their work shows that the $\text{He}(2S)/H_2O$ interaction is highly anisotropic. $\text{He}(2S)$ atoms encounter a repulsive wall when approaching $H_2O$ molecules from the hydrogen side, but a sizeable attraction when approaching from the oxygen side.

The EED and polarization profile for $SO_2$ are shown in Fig. 2(b). In contrast to $H_2O$, $SO_2$ has a positive electron affinity ($-1.1 \text{ eV}$) making possible ionization via the ionic channel. The two, relatively narrow high-energy features at $\sim 6.3$ and $7.2 \text{ eV}$ in the EED distribution, however, result from ionization via the ionic channel and correspond to formation of $SO_2^-$ ions in $^2A_1(6\sigma_g^+)$, $^2A_1(1\pi^2 

\downarrow$).

The measured electron polarization in this energy range are large suggesting that ionization is dominated by Auger-type processes. Such processes, which require that an electron tunnel from the $SO_2$ target molecule into the $\text{He}(2S)$ $1s$ core hole, can only take place at relative small $\text{He}(2S)/SO_2$ separations. A fraction of the collision partners must, therefore, be able to survive the crossing with the $SO_2^-$ ionic potential which occurs at somewhat larger separations. This is consistent with the conclusion of Goy et al.\textsuperscript{12} that electron transfer is symmetry forbidden if the $\text{He}(2S)$ atom is in the plane of the $SO_2$ molecule when it reaches the crossing radius.

The broad, low-energy part of the EED is associated primarily with ionization via ionic channels. In this energy regime, the electron polarization decreases substantially, presumably as a result of spin-orbit coupling. Reactions via the ionic channel can be loosely pictured as proceeding through transfer of the $\text{He}(2S)\quad 2p$ electron to produce a $\text{He}^+\quad SO_2^-\quad$ ion pair. The electron is captured into a non-degenerate $5\sigma$ orbital for which the orbital electronic angular momentum would be zero if the $SO_2^-$ ion was isolated, in which case the polarization of the "captured" $2p$ electron would not be disturbed by spin-orbit coupling before being ejected from the collision complex by autoionization into final $\text{He}(1S)+SO_2^++e^-$ states. For much of the collision, however, the $SO_2^-$ ion will in fact be strongly perturbed by the nearby $He^+$ ion and it is, therefore, not possible to infer the behavior of the attached electron simply by considering the properties of isolated $SO_2^-$ ions. In particular, hybridization effects introduced by interaction with the $He^+$ ion might induce a time-dependent electron orbital moment and this could lead to significant spin-orbit effects. The decrease in polarization observed with decreasing electron energy might then be explained qualitatively by noting that lower electron energies typically correlate with ionization at smaller internuclear separations, which might allow stronger spin-orbit coupling and a larger decrease in polarization. Alternately, the $He^+\quad SO_2^-$ ion pair might also decay through formation of $SO_2^+$ excited states that may subsequently autoionize or that may dissociate yielding excited $O^+$ and $S^+$ atoms, which have been detected through fluorescence.\textsuperscript{13} Excitation transfer will populate triplet $SO_2^+$ states and spin-orbit effects could again degrade the electron polarization prior to autoionization.

The peak in the EED for $SO_2$ at $-3 \text{ eV}$ is associated with contributions to the total electron signal that result from ionization via the covalent channel to form $SO_2^+$ ions in principally the $^2B_1(6\sigma_g^+)$ and $^2A_1(5\pi^2 

\downarrow$) states.\textsuperscript{12,13} (A large fraction of these ions subsequently dissociate forming $SO^+$ and $S^+$.) Such a contribution to the total electron signal is consistent with the local maximum in electron polarization observed in the same energy range. Indeed, the $3\sigma_g$ and $5\pi$ orbitals have sizable electron densities in the molecular plane [the preferred location of the $\text{He}(2S)$ atom for covalent ionization] thereby facilitating Auger-type processes.

The EED for $NO$ shown in Fig. 2(c) contains a number of sharp features that correspond to ionization into excited $a^2\Sigma^+\quad (2p\pi^-)$, $b^3\Pi(2p\pi^-)$, $c^3\Pi(2p\pi^-)$, and $A^3\Pi(2p\pi^-)$ states of the product $NO^+$ ion.\textsuperscript{14} Ionization into the ground $X^2\Sigma^+\quad (2p\pi^+-)$ state produces electrons with energies near $10 \text{ eV}$, but insufficient electrons could be extracted from the afterglow at these energies to permit a reliable polarization measurement. The presence of sharp features in the EED is indicative of ionization from the covalent entrance channel; indeed, it is even possible to distinguish population of different vibrational states of the product ions. $NO$, however, has a small positive electron affinity, $-0.03 \text{ eV}$, and some of the underlying background in the EED might result from ionization via ionic channels. Although it is clear that a substantial fraction of the ionization must result from covalent channels, the measured electron polarization are quite low. This can be explained, however, because, unlike $H_2O$ or $SO_2$, NO is an open shell molecule, which makes possible exchange between the He $2s$ and NO $2p\pi^-$ electrons. The possible initial spin states for the reactants are

$$\text{He}(2S)\left< 1s \right> + NO\left< 1S \right> \rightarrow \text{He}(1S)\left< 1S \right> + NO^+\left< 1S \right> + e^-\left< 1S \right> \quad (3a)$$

$$\text{He}(2S)\left< 1s \right> + NO\left< 1S \right> \rightarrow \text{He}(1S)\left< 1S \right> + NO^+\left< 1S \right> + e^-\left< 1S \right> \quad (3b)$$

The reacting system can form both doublet and quartet spin states and the two $\{M_2(\text{He}), M_2(\text{NO})\}$ entrance
channels can be expressed in terms of the \( |S, M_S \rangle \) states for the total system as \( |1, 1/2 \rangle = |3/2, 3/2 \rangle \) and \( |1, -1/2 \rangle = 1/\sqrt{2} (|3/2, 1/2 \rangle + |1/2, 1/2 \rangle) \). Consider initially ionization via the covalent channel, which might be expected to proceed simply through tunneling of an NO 2p or 2p* electron into the 2S 1S core hole (the NO+ ions of interest are formed in excited states) with simultaneous ejection of the 2s 1S electron. Case (3a) then leads to the formation of triplet NO+ ions in the \( M_S(\text{NO}^+) = +1 \) state, whereas case (3b) allows production of NO+ ions in both singlet and triplet states, but with \( M_S(\text{NO}^+) = 0 \).

Despite this, in each case the polarization of the ejected electrons will equal that of the 2S atoms. The situation is changed dramatically for case (3b), however, if, as the collision partners approach, exchange occurs between the He 2s 1S electron and the NO 2p** 1S electron because tunneling then leads to the ejection of a 2s 1S electron. Since the product ion must be left in an \( M_S(\text{NO}^+) = +1 \) state, only triplet NO+ ions can be formed in this manner. While it is not possible to calculate the probability for exchange, it is evident that for open-shell molecules such as NO ionization via the covalent channel need not lead to the production of highly polarized electrons. In essence, the polarization of the 2S atoms is degraded by exchange before ionization occurs. Production of singlet NO+ ions allows only doublet final states for the system. Reaction is therefore only possible for case (3b) and the product electrons must be fully polarized. The polarization maximum observed at energies of about 1.5 eV can be attributed to contributions to the total electron signal associated with production of NO+ ions in \( A^2\Pi \) states.

Ionization via the ionic channel, if it occurs, can also lead to a decreased electron polarization. Capture of a He(2S 1S) 2s electron into the NO 2p** orbital results in the formation of NO+ ions in the \( 2^+ \) state, and the resulting He++NO collision complex admits both doublet and quartet spin states. For case (3a), the NO+ ions are formed in the \( M_S(\text{NO}^+) = +1 \) state. In the absence of spin-orbit coupling, subsequent autoionization of the collision complex must result in the ejection of a 2p** electron and in the production of fully polarized electrons. In case (3b), electron capture forms NO+ ions the \( M_S(\text{NO}^+) = 0 \) state, and autoionization can result in the ejection of either an 1 or 2p** electron. If it is assumed that the probability that an electron be ejected from the 2p** orbital is independent of its spin, case (3b) will lead to product electrons with zero net polarization. Thus if cases (3a) and (3b) are equally likely, ionization via the ionic channel will lead to the production of electrons with 50% polarization. This could, however, be reduced by spin-orbit coupling. Although the NO+ ions are formed in \( 2^+ \) states having no electronic orbital moment, perturbations introduced by the nearby He+ ion might induce a net orbital moment as in the case of SO2 discussed previously. Spin-orbit coupling could then, in case (3a), degrade the 2p** electron polarization prior to autoionization and decrease the overall ejected electron polarization.

The EED for NO2, shown in Fig. 3(d), comprises a broad relatively featureless background associated with ionization via ionic channels (NO2 has a sizable electron affinity, \( \sim 2.4 \) eV) superimposed upon which are a number of sharp peaks corresponding to ionization from the covalent entrance channel into the \( 3^1B_1(4e^{-}) \), \( 3^3A_4(1e^{-}) \), and \( 1^3B_2(3e^{-}) \) states of the NO2+ ion. Since covalent ionization can occur only at relatively small separations, this requires that a fraction of the collision partners is able to survive the crossing with the He++NO2+ ionic potential.

This is to be expected because the coherent neutral collision partners He(2S 1S) and NO2(\( A^2\Pi \)), can form either doublet or quartet spin states whereas the He++(3S)+NO2+ (\( A^2\Pi \)) system allows only doublet spin states. Thus reactions via the ionic channel are spin forbidden for the quartet entrance channel. Spin conservation, however, requires that (covalent) reactions via the quartet channel produce triplet NO2+ ions, as is observed. The large polarization measured in the vicinity of the \( 3^3B_1(4e^{-}) \) and \( 3^3A_4(1e^{-}) \) features is consistent with ionization via the covalent channel, although the polarization may be degraded somewhat as the result of exchange (NO2 is an open-shell molecule). The local maximum in polarization observed at energies below \( \sim 2 \) eV may be attributed to contributions to the total electron signal associated with population of NO2+ 3^3B_1(3e^{-}) and (possibly) 3^3B_1(1e^{-}) and 3^3A_4(5e^{-}) states via the covalent channel.

The pronounced decrease in electron polarization observed at energies below \( \sim 4.5 \) eV coincides with the increase in electron signal attributed to ionization via the ionic channel. Because electron transfer must form NO2+ ions in the \( A^2\Pi \) state, autoionization of the resulting He++NO2+ collision complex may then be accompanied by ejection of either an 1 or 2p** electron. Assuming that each is equally probable, ionization via the ionic channel will give electrons with zero polarization. This would explain the very low polarization measured at energies near 3 eV where there is only a small contribution to the total electron signal from the covalent channel.

The present data show that spin-labeling techniques provide a novel approach to study the dynamics of PI reactions and can reveal the existence of exchange and spin-orbit effects that cannot be observed simply through measurements of the EED’s of ejected electrons.

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 Defined as \((n_2 - n_1)/(n_1 + n_2 + n_3)\), where \(n_1\), \(n_2\), and \(n_3\) are the numbers of \(2\) \(S\) atoms in the \(M_2(M_3) = 4\) \(0\), and \(-1\) levels, respectively.

Defined as \((n_1 - n_2)/(n_1 + n_2 + n_3)\), where \(n_1\) and \(n_2\) are the numbers of electrons with \(m_\pi = 1/2(1)\) and \(-1/2(-1)\), respectively.


Spin correlation in Auger neutralization of He\(^+\) ions at a Cu(100) surface

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Energy distributions of electrons ejected from an atomically clean Cu(100) surface by incident thermal-energy helium 2\(^S\), 2\(^P\), and 2\(^P\) atoms are presented, which show that each species is deexcited exclusively through resonance ionization followed by Auger neutralization. These data, when coupled with earlier measurements in this laboratory using electron-spin-polarized He (2\(^S\)) atoms, require that the electrons involved in the Auger neutralization process tend to have antiparallel spins. This work provides direct confirmation of spin correlation in Auger neutralization of ions outside a paramagnetic surface.

Recent experiments have shown that the dynamics of He(2\(^S\)) metastable atom deexcitation at surfaces can be explored by use of spin-labeling techniques in which electron-spin-polarized He(2\(^S\)) atoms are directed at the target surface and the polarization of the ejected electrons is measured.\(^1,2,3\) Such investigations have revealed that, contrary to initial expectations, the electrons ejected from clean paramagnetic metal surfaces such as Cu(100) (Ref. 3) by polarized He(2\(^S\)) atoms have a significant spin polarization, which reflects that of the incident atoms. Conventional models\(^4\) suggest that He(2\(^S\)) atoms will be deexcited at surfaces of sufficiently high work function such as Cu(100) exclusively by the two-step process diagrammed in Fig. 1(a). The 2\(^S\) atom first undergoes resonance ionization (RI) in which the excited 2s electron tunnels into an unoccupied level above the Fermi surface. The resulting He\(^+\) ion continues toward the surface, where it is neutralized by a conduction electron from the metal, with the released energy being communicated to a second (Auger) electron, which may, if the transferred energy is sufficiently large, be ejected from the surface. In this process, termed Auger neutralization (AN), it is an electron from the metal that is ejected, and the polarization observed from Cu(100) would imply that the electrons involved in the AN process tend to have antiparallel spins, thereby favoring singlet two-hole final states in the target. An alternate explanation, however, has also been examined,\(^5\) which suggests that, because of hybridization, the He(2\(^S\)) resonance ionization rate might saturate, allowing a significant number of the incident 2\(^S\) atoms to survive passage to regions close to the surface where they might be deexcited by Auger deexcitation (AD) process illustrated in Fig. 1(b). In this case an electron from the metal tunnels directly into the He(2\(^S\)) is core hole with simultaneous ejection of the (polarized) excited 2s electron. Such behavior could clearly account for the observed polarization without requiring any spin correlation in the AN process. In this work we determine which mechanism accounts for the observed polarization by comparing directly the energy distributions of electrons ejected from a Cu(100) surface by helium 2\(^S\), 2\(^P\), and 2\(^P\) atoms. The data show that each species is deexcited exclusively through RI+AN, which, when coupled with the earlier observations using polarized He(2\(^S\)) atoms, requires that AN of He\(^+\) ions at a Cu(100) surface favors singlet two-hole final states. This work provides the first direct confirmation of spin correlation in Auger neutralization of ions at a surface.

The present apparatus is shown schematically in Fig. 2 and has been described elsewhere.\(^1,4\) Briefly, a fraction of the atoms contained in a ground-state helium-atom beam formed by a multichannel array is excited to the 2\(^S\) metastable levels by a coaxial electron beam. The 2\(^S\) atoms may be removed from the beam by illuminating it with 2.06-\(\mu\)m radiation from a helium quench lamp, which excites 2\(^S\) \(\rightarrow\) 2\(^P\) \(\rightarrow\) 1\(^S\) transitions. Charged particles formed by electron impact are removed by a transverse electric field. A mechanical chopper is used, in conjunction with time-of-flight techniques, to discriminate against electron ejection by photons or fast ground-state atoms that might be produced in the source. The He(2\(^S\)) atoms used in this study are created by illuminating the He(2\(^S\)) beam with 1.06-\(\mu\)m 2\(^S\) \(\rightarrow\) 2\(^P\) radiation from a single-mode frequency-stabilized Coherent Inc. 899-21 Ti-sapphire laser. (The laser beam is incident normal to the 2\(^S\) beam to minimize the effective Doppler width of the transition.) The laser was

![FIG. 1. Schematic diagram of the electron ejection processes that can occur when He(2\(^S\)) atoms are deexcited at a clean metal surface.](image)
specially optimized for operation at long wavelengths and provides ~300 mW at 1.08 μm with 21 W all-line Ar+ ion laser pumping. As will be discussed, this output power is more than sufficient to saturate the 2P (2P) transition and make possible the study of collision processes involving He(2P) atoms that can provide new insights into the dynamics of excited-atom deexcitation at surfaces. In the present study, the laser beam is incident at the target surface because the lifetime of the 2P level (~0.1 μsec) is such that, once created, a 2P atom will (in the absence of stimulated emission) typically travel ≤0.2 mm before decay. The energy distribution of electrons ejected from the target surface by the incident excited atoms is measured using a retarding-potential energy analyzer that has an energy resolution of ~0.6 eV.

The Cu(100) sample was mounted on a LHe-cooled Dewar and was cleaned by repeated cycles of 500-eV Ar+ ion bombardment followed by annealing to ~800 K. Surface cleanliness and order were monitored by Auger emission spectroscopy (AES) and low-energy electron diffraction (LEED), respectively. Sputtering-annealing cycles were continued until surface contamination levels were below the Auger detection limit and a sharp LEED pattern was obtained.

Initially, tests were undertaken to confirm that the laser was able to saturate the 2S → 2P transition. In these experiments the Cu(100) surface was cooled to ~25 K and exposed to 50 L of CO2 (sufficient to build up a condensed CO2 film several monolayers thick). The energy distribution of electrons ejected from the film by an incident 2S beam is shown in Fig. 3(a), together with the energy distribution observed (with higher-energy resolution) in earlier gas-phase Penning ionization (PI) studies. The general characteristics of the two distributions are similar, indicating that, in essence, electron ejection from the film occurs through PI of adsorbed molecules, a process termed surface PI. (As indicated in Fig. 3, the various peaks evident in the energy distributions are associated with population of the ground 3P1 and excited 3P2 and 4P states of the product CO2+ ion.)

Besides using spin-polarized He(2S) atoms to show that the polarization of the ejected electrons is equal to that of the 2S atoms, this, electron ejection must occur via an AD-type process in which an electron from a CO2 molecule in the condensed film tunnels into the vacant He(2S) hole with simultaneous ejection of the excited 2P electron.

The electron-energy distribution obtained with the laser beam illuminating the film is presented in Fig. 3(b). It is evident that, although the total ejected electron signal remains essentially constant, the presence of 2P atoms causes a marked change in the electron-energy distribution. These changes are emphasized in Fig. 3(d), which shows the difference between the energy distributions obtained with and without the laser beam present. Laser illumination results in the appearance of higher-energy features in the energy distribution and a decrease in the size of those features associated with ejection by 2S atoms. Subtraction of the signal due to the remaining 2S atoms from the energy distribution in Fig. 3(b) provides the energy distribution characteristic of ejection by 2P atoms and is presented in Fig. 3(c) (normalized to the same ejected electron yield as Fig. 3(a)). The distributions for 2S and 2P atoms are similar except that for 2P atoms they are shifted toward higher energies by ~1-1.2 eV. Because the 2P level lies 1.14 eV higher in energy than the 2S level, this suggests that electron ejection by 2P atoms also results from surface PI. An electron from a CO2 molecule in the condensed film fills the vacant He(2P) hole with simultaneous ejection of the excited 2P electron.

To check for saturation of the 2S → 2P transition, data were recorded with a variety of neutral density filters introduced in the laser beam. Figure 3(d) includes the difference between the laser-on and laser-off energy distributions obtained with the laser intensity reduced by a factor of 2. This difference is very similar to that observed with the unattenuated laser beam indicating that the laser is able to saturate the 2S → 2P transition. Indeed, measurements showed that the electron signal at energies above ~7.2 eV (due solely to ejection by 2P atoms) decreased by less than 30% upon reducing the incident laser intensity by an order of magnitude.

The electron-energy distribution resulting from He(2S) deexcitation at a clean Cu(100) surface is presented in Fig. 4(a), together with that observed when the laser was used to saturate the 2S → 2P transition. The difference between these two distributions is shown in Fig. 4(b), and it is apparent that, to within experimental error, they (and the total electron yield) are identical. In particular, detailed studies showed that at energies above 12 eV the ejected electron signal changed by less than 1% upon laser illumination. Measurements with the quench lamp turned on and off were also undertaken to obtain the energy distribution associated with 2S deexcitation. The 2S level lies 0.80 eV above the 2P level.) This distribution is included in Fig. 4(a) (normalized to the same ejected electron yield as the 2S and 2P data) and is again identical to that for 2S (and 2P) atoms. It is apparent that the increased internal energy associated with 2S and 2P atoms does not lead to any significant changes in the ejected electron energy distribution. This can only be explained if, in each case, deexcitation occurs exclusively through R1+AN, i.e., the tunneling rates associated with R1 of 2S, 2S, and 2P atoms must be such that for each incident atom is converted to a He+ ion prior to electron ejection occurring. The alternate possibility,
FIG. 3. Ejected electron-energy distributions resulting from the deexcitation of (a) $\text{He}^2(2\,^5S)$ atoms, (b) $\text{He}^2(2\,^5S)/\text{He}^2(2\,^3P)$ mixture, and (c) $\text{He}^2(2\,^3P)$ atoms at a condensed CO$_2$ film. The electron energy distribution (---) resulting from gas-phase Penning ionization of CO$_2$ is also included in (a). (d) Difference between the energy distributions measured with mixed $\text{He}^2(2\,^5S)/\text{He}^2(2\,^3P)$ and pure $\text{He}^2(2\,^5S)$ atom beams using full (\textcircled{V}) and reduced (50\%) (O) laser intensities.

FIG. 4. (a) Ejected electron-energy distributions resulting from deexcitation of $\text{He}^2(2\,^5S)$ atoms (---), a $\text{He}^2(2\,^5S)/\text{He}^2(2\,^3P)$ mixture (---), and $\text{He}^2(2\,^5S)$ atoms (---) at an atomically clean Cu(100) surface. *,, ejected electron polarizations measured in earlier studies using polarized $\text{He}^2(2\,^5S)$ atoms. (b) Difference between the energy distributions measured with mixed $\text{He}^2(2\,^5S)/\text{He}^2(2\,^3P)$ and pure $\text{He}^2(2\,^5S)$ atom beams.

namely, that incident $2\,^1S$ and $2\,^3P$ atoms are all converted to $2\,^1S$ atoms during approach to the surface through a process analogous to that observed at low work function surfaces, can be ruled out because even at relatively large distances (\~10 Å) from a Cu(100) surface the $2\,^1S$ level lies well above the Fermi level. Therefore, even though calculations indicate that the R1 tunneling rates for $2\,^3P$ states are significantly higher than for $2\,^1S$ states, the tunneling rate for $2\,^1S$ states must, nonetheless, be sufficient to ensure that no $2\,^1S$ atoms survive passage to regions sufficiently close to the surface that AD can occur.

The ejected electron polarizations observed in earlier studies of Cu(100) using polarized $\text{He}^2(2\,^5S)$ atoms are included in Fig. 4(a). (The electron polarization is expressed as a percentage of the incident $2\,^5S$ atom polarization.) Since this work shows that $2\,^1S$ deexcitation occurs exclusively through R1+AN, the measured electron polarization requires that the electrons involved in the AN process tend to have antiparallel spins. This is evident from Fig. 1(a): the $\text{He}^+$ hole must be filled by a spin-down electron (the helium ground state is a spin singlet), but, as shown by experiment, this is accompanied by the preferential ejection of a spin-up electron. The formation of singlet two-hole final states at the sur-
face is therefore favored. The observed spin correlation is quite large, especially at the highest ejected electron energies for which both electrons must originate near the Fermi level.

Superficially similar spin-correlation effects have been observed in Auger processes originating on core holes inside narrow band metals and are interpreted in terms of two-hole localization. Such final states can be formed when the Coulomb repulsion between the two holes is larger than the bandwidth of the metal and result in predominantly singlet two-hole states bound to the same core site. Transitions into such states will be narrow and atomiclike. Clearly, this picture does not apply to the present experiments in which the He $^4$ Is "core hole" is outside the target surface. Rather, a recent theoretical analysis suggests that the spin correlation reported here arises primarily because interference effects between direct and exchange Auger processes diminish the likelihood of triplet two-hole final states. 12

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3This earlier work also showed that Pd(110), Fe(110), and Si(100) exhibit spin-correlation behavior similar to that of Cu(100).
Absolute calibration of a Mott polarimeter using surface Penning ionization

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A technique for absolute calibration of a Mott polarimeter is described that makes use of electrons of accurately known polarization obtained through surface Penning ionization. This approach provides higher count rates and lower uncertainties than obtained in earlier measurements based on gas-phase Penning ionization.

Recently we described a technique for the absolute calibration of a Mott polarimeter that made use of electrons of accurately known polarization obtained through gas-phase Penning ionization (PI) reactions involving electron-spin-polarized He(2S) metastable atoms. In the present note we describe a variant of this technique in which the electrons used in calibration are produced by PI of Xe atoms adsorbed on a cooled copper surface. This approach results in much higher count rates and reduced uncertainties, and has been used to calibrate a compact Mott polarimeter that incorporates an in-line retarding-grid energy analyzer.

The present apparatus is similar in many respects to that used earlier. A fraction of the atoms contained in a ground state helium atom beam are excited to the 2S levels by coaxial electron impact. The 2S atoms are removed from the beam by illuminating it with 206-μm radiation from a helium discharge lamp which excites 2S→2P transitions. A weak (~0.5 G) magnetic field is established perpendicular to the beam axis to provide a well-defined quantization axis. Circularly polarized 1.08-μm 2S→2P2 radiation from a frequency-stabilized Coherent Inc. CR 899-21 Ti:sapphire laser is incident parallel to the magnetic field and is used to optically pump the 2S atoms to increase the relative populations in the M(2S) = +1 or -1 magnetic sublevels. The resulting beam polarization, \( P_b \), which is accurately measured using a Stern-Gerlach (SG) analyzer, is much higher than obtained previously by optical pumping using radiation from a high-power helium lamp, a consequence of the much higher spectral brightness of the laser. (The laser was specially optimized for operation at long wavelengths and provides ~300 mW at 1.08 μm with 2-W all-line Ar laser pumping.) The polarization of the atoms can be simply reversed \( P_b \rightarrow -P_b \) by changing the sense of circular polarization of the optical pumping radiation. A mechanical chopper and time-of-flight techniques are used to discriminate against photons and fast neutrals produced in the metastable atom source.

The metastable atoms are deexcited through interactions with Xe atoms adsorbed on a Cu(100) surface cooled to ~35–40 K, resulting in electron ejection. The energy distribution of the ejected electrons was essentially independent of surface exposure over a wide range (~5–100 L) and contained two sharp, well-resolved high-energy (~8 eV) peaks separated by ~1.3 eV similar to those observed in gas-phase PI studies. This suggests that the electrons that make up these peaks result from PI of adsorbed Xe atoms through reactions of the type

\[
\text{He}(2S) + \text{Xe} + e^{-} \quad \text{He}(1S) + \text{Xe} + e^{-}
\]

which, because spin is conserved, lead to the production of free electrons whose polarization \( P \) is equal to that of the Xe atoms. No significant ejected electron signal was observed in a broad energy interval below the two PI peaks. This indicates that the production of (unpolarized) secondary electrons by Penning electrons that are initially directed into the surface must be small and that such electrons cannot provide a significant contribution to the observed peaks. Nonetheless, to minimize the possibility of systematic error associated with such secondary electron production, data were typically recorded using only those electrons in the higher energy peak which were selected by application of an appropriate bias to the retarding grids in the energy analyzer. No systematic differences were apparent; however, between results obtained under these conditions and under conditions where electrons from both peaks were admitted by the energy analyzer. To further test the hypothesis that spin polarization is fully conserved in surface PI, measurements were also undertaken using CO2 gas-phase PI reactions with CO2 conserve spin. The energy distribution of the ejected electrons were again similar to that observed in gas-phase PI studies. No systematic differences were observed between polarimeter calibrations undertaken using electrons in the higher-energy CO2 surface PI peaks and using Xe. In addition, studies with CO2 showed that, for identical He(2S) beam polarizations, the scattering asymmetries measured in the polar-
imeter using electrons from gas-phase PI and from the higher-energy surface PI peaks were equal to within ±1%. (Similar tests could not be undertaken using Xe due to its smaller gas-phase PI cross section.) However, the surface PI currents obtained with CO₂ and Xe are similar because the incident metastable atoms are deexcited with essentially unit probability. It is therefore reasonable to conclude that for both Xe and CO₂ the polarization of electrons resulting from surface PI equals the (known) polarization of the 2S atoms and (for the higher-energy features) is not degraded by secondary-electron production.

The Mott polarimeter has been described elsewhere. Incident electrons, after passing through the in-line retarding-grid energy analyzer, are accelerated and focused by a three-element electrostatic lens onto a thick Thorium target maintained at +20 kV. Electrons quasi-elastically scattered through ±120° at the target are decelerated in a retarding field and are detected by two bell-mouthed channellectrons. The maximum inelastic energy loss that an electron can suffer and still be detected, i.e., the inelastic energy loss window ΔE, is determined by the retarding field and the bias applied to the channeltron cones. The left-right scattering asymmetry A defined as (N_L - N_R)/(N_L + N_R) where N_L and N_R are the scattered electron count rates in the left and right detectors, respectively, is related to the component of electron polarization perpendicular to the scattering plane (which for the present geometry is simply P = P_L/P_R) by the relation A = PΔE, where ΔE is the effective asymmetry (Sherman) function. Thus, given P, measurement of A yields the value of ΔE appropriate to the particular operating conditions in use. In practice, however, the counting rates in the left and right detectors are influenced by instrumental asymmetries associated with unequal detector responses, collection solid angles, etc. Such asymmetries were identified and eliminated by undertaking additional measurements with the input beam polarization reversed (P — P), allowing accurate determination of ΔE.

The polarimeter was calibrated under normal operating conditions (ΔE = 1.3 keV, P = 0.95 ± 0.02) yielding the value SΔE = 0.110 ± 0.003. This is in agreement with the value obtained earlier using electrons produced in gas-phase PI reactions, but the experimental uncertainty is significantly reduced. Surface PI results in higher electron currents than can be obtained through gas-phase PI and this, coupled with the larger asymmetries that result from the higher beam polarizations afforded by the Ti:sapphire laser, leads to lower statistical uncertainties. The high beam polarization also reduces the effects of possible systematic errors associated with measurement of the 2S polarization using the SG analyzer. The present method yields calibration accuracies that are better than those typically associated with foil-thickness or inelastic-energy-loss extrapolation techniques and is not reliant on calculated scattering asymmetries.

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4 Defined as P = (n_p - n_n)/(n_p + n_p + n_n), where n_p, n_n and n_p are the number of atoms in the beam with M_0/M_2 = 1.0, and
5 −1, respectively.
8 Similarities between surface and gas-phase PI reactions have been noted previously. See, for example, Y. Harada and H. Ozaki, Jpn. J. Appl. Phys. 26, 1201 (1987).
10 Defined as P = (n_p - n_n)/(n_p + n_n), where n_p and n_n are the number of electrons with m = ±1/2 and —1/2, respectively.
12 See, for example, J. Kuster, Polymorphic Electrons, 2nd ed. (Springer, Berlin, 1983).
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(2^1S) 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(2^1S) atoms. Results obtained using CO₂, CO, Cl₂, and O₂ target gases are presented that illustrate the capabilities of this approach. In particular, the data for Cl₂ and O₂ 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

$$\text{He(2}^1\text{S}) + \text{M} \rightarrow \text{He(1}^\text{S}) + \text{M}^+ + e^-$$

(1)

involving He(2^1S) metastable atoms and some atomic or molecular target 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(2^1S) + M entrance potential to the final He(1^S) + 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 He^+ + 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(2^1S) atoms coupled with energy-resolved spin analysis of the product electrons, can provide further insight into the dynamics of PI reactions. Data obtained with CO₂, CO, Cl₂, and O₂ 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(2^1S) atoms in a flowing helium afterglow which are optically pumped to populate preferentially either the $M_J(M_F)^+=+1$ 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(2^1S) atoms with negligible He(2^3S) 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 ≤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 1.063 μm 2^3P₁ → 2^3S₁ radiation from a single-mode, frequency-stabilized lanthanum neodymium magnesium hexafluoride (LNAl) laser [4] with subsequent spontaneous decay back to the 2^3S level. The laser beam is incident parallel to a weak (~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 O₂, the measured electron energy distributions

![FIG. 1. Schematic diagram of the apparatus.](image-url)
(EED's) and polarizations were insensitive to target-gas flow rate over a wide range. For O₂, low flow rates are used to ensure that the electron polarization is not degraded through exchange in e⁻–O₂ 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 polariometer operating at 20 kV is used to measure the electron polarization [3].

Prior to each data acquisition run, the polarization [6] \( P_e \) 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

\[
\text{He}(2^3S) + \text{Ar}(1^S) \rightarrow \text{He}(1^S) + \text{Ar}^+(2^3P) + e^- \text{[1]}.
\]

Thus, since the polarization of the product electrons is equal to that of the 2 ³S atoms, \( P_e \) 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 ~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 desorbed 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 CO₂, CO, C₂H₂, and O₂ 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 CO₂ 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 \( C^2 \Sigma_u^+ \) states of the product CO₂⁺ ion, i.e., to removal of an electron from the CO₂ 1π<sub>g</sub>, 1π<sub>u</sub>, 3σ<sub>g</sub>, and 4σ<sub>u</sub> 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 \( \Sigma \) states is most favorable for collinear end-on collisions, whereas side-on collisions are more effective for ionization into \( \Pi \) states)

**FIG. 2.** Electron-energy distributions and polarization profiles measured following PI reaction with (a) CO₂, (b) CO, (c) C₂H₂, and (d) O₂. \( \Pi \), electron polarizations; \( \sigma \), measured energy distributions; \( \bullet \), energy distributions obtained by earlier workers using beam and gas cell techniques.
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 insignificant.) PI reactions with CO must therefore proceed by an Auger-type process in which an electron of appropriate spin from the target molecule tunnels into the 1s hole in the 2S atom with simultaneous ejection of the 2S electron.

The EED associated with the PI of CO again comprises a series of relatively sharp features, which correspond primarily to the $X^2^\Sigma^+$, $A^2^\Pi$, 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 2S atom. The polarization of the (smaller) $A^2^\Pi$ feature appears to be slightly lower but this may be attributed in part 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 $\approx 5.4$ eV results from ionization via the covalent channel into the Cl$_2^+$, $A^2^\Pi$, state. Smaller features at $\approx 8.2$ and $3.7$ eV associated with ionization into Cl$_2^+$, $X^2^\Pi$, and $B^2^\Sigma^+$ 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 2S 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 $\approx 2.7$ eV, can be reproduced by modeling both the particle trajectories in the collision complex and the partial widths for ionization 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$^1^S^+(3p^5D$in)), which, if the energy of core excitation (1.45 eV) is greater than the binding energy of the $n$J electron, can undergo autoionization. The peak in the EED immediately below $\approx 1.45$ eV is attributed to such autoionization [12].

The polarization of those electrons that comprise the $A^2^\Pi$ peak is allowing for possible small contributions from surface ejection, equal to that of the 2S atom, 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 electron to produce a He$^+$ + Cl$_2^+$ ion pair. Electron attachment to Cl$_2$ results in Cl$_2^-$ ions in the $2^\Sigma^-$ state, suggesting that the polarization of a "captured" 2s 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 $\approx 1.5$ eV is associated with contributions to the electron signal from autoionization of excited CI$^1^+$[3p$^5D$ in]] atoms. Such autoionization produces CI$^+$ ions in $^3P$ states and must therefore occur via an exchange process in which the $nl$ electron is captured in the core ejecting a 3p electron. Thus, a reduction in the electron polarization is expected (the 3p electrons are unpolarized). Indeed, the observation of a pronounced polarization minimum confirms the importance of CI$^1^+$ autoionizing states. No simple explanation for the polarization minimum at $\approx 2.8$ 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 $X^2^\Pi$, $A^2^\Pi$, and $B^2^\Sigma^+$ states of the O$_2^+$ ion [13]. The measured electron polarization values are much smaller than for the other targets studied in this work, and even the $X^2^\Pi$, covalent channel does not result in a large electron polarization. This is not unexpected, because (unlike CO, CO$_2$, and Cl$_2$) O$_2$ is an open-shell molecule, and the polarization of the incoming 2S atom can be degraded prior to ionization by exchange between the He 2S and O$_2$ 1S electrons. The low polarization associated with ionization via ionic channels can be explained by considering the possible spin states for the reactants, which are

$$\text{He}(2^2\Sigma)(1)+\text{O}_2(\cdots 3p^5 1\text{S}_0^+ 1\text{S}_0^+) \text{[11]}$$

$$\text{[11]} \text{[3a]}$$

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 $|M_2(\text{He})_2 M_2(\text{O}_2)\rangle$ entrance channels can be expressed in terms of the possible $|S, M_2\rangle$ states for the total system as $|1,1\rangle = (2,2)$; $|1,1\rangle = (1,\sqrt{2}) (2,1)$.
+1, 1\rangle; \quad |1, -1\rangle = (\sqrt{6}) |2, 0\rangle + (\sqrt{2}) |1, 0\rangle + (\sqrt{3}) |0, 0\rangle. \] Thus, since reaction from the quencher entrance channel is spin forbidden, reaction will not occur for case (3a); for case (3b), reaction will proceed, on average, in only 1 of the collisions, while for case (3c), reaction is possible in 1 of the collisions. Energy conservation requires that the portion of the EED above 4 eV correspond to ionization into the \( \Omega_2^+ \chi^2 \Pi_g \) ground state, whereupon, assuming that the probability that an electron be ejected from the \( \Omega_2^- 1 \Pi_g \) 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 \( \text{He} 2s \) and \( \Omega_2 1 \Pi_g \) 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 \( \Omega_2^+ \) states must be considered. In such reactions, the electron that tunnels into the \( \text{He} 1 \Pi_g \) core hole must originate from the \( \Omega_2^- 1 \Pi_g \) 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 \( \Omega_2^+ \) \( b^4 \Sigma_g^- \) and \( \sigma^4 \Pi_g \) final states via the covalent channel, with underlying contributions from ionic channel ionization into both ground and excited \( \Omega_2^+ \) states.

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[6] Defined as \( n_+ = n/2, n_0 + n_+ - 1 \), where \( n_+ \), \( n_0 \), and \( n_- \) are the numbers of \( 2 \sigma^2 \) atoms in the \( M_f M_g = +1, 0 \), and \( -1 \) levels, respectively.


[8] Defined as \( n_+ = n/2(n_+ + n_-) \), where \( n_+ \) and \( n_- \) are the numbers of electrons with spin "up" and "down" relative to the quantization axis.


Use of spin-labelling techniques to probe the dynamics of $\text{He}(2^3S)$ deexcitation at solid surfaces

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Abstract. Spin labelling techniques, specifically the use of electron-spin-polarized $\text{He}(2^3S)$ metastable atoms coupled with energy-resolved spin analysis of the ejected electrons, are used to investigate the dynamics of $\text{He}(2^3S)$ deexcitation at solid surfaces. Data for a clean Au(100) surface are presented that show that deexcitation occurs exclusively through resonance ionization followed by Auger neutralization. The electrons involved in Auger neutralization are observed to be correlated in spin and possible reasons for this are discussed. Results obtained at Xe and NO films adsorbed on cooled Au(100) and Cu(100) substrates, respectively, show that $\text{He}(2^3S)$ metastable atom deexcitation is analogous to gas-phase Penning ionization. Detailed differences are apparent that can be attributed to effects associated with the underlying substrate and interactions involving neighboring atoms in the film.

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Recent work in this laboratory has shown that spin-labelling techniques provide a powerful means to investigate the dynamics of reactions involving $\text{He}(2^3S)$ atoms. This approach complements earlier studies of reaction dynamics that were based solely on analysis of the energy distributions of product electrons. Here we focus on the use of spin-labelling techniques to probe the dynamics of $\text{He}(2^3S)$ atom deexcitation at clean and adsorbate-covered surfaces [1, 2]. Conventional models [3] suggest that $\text{He}(2^3S)$ atoms will be deexcited at clean high-work-function metal surfaces exclusively by the two-step process diagrammed in Fig. 1a. An incident $2^3S$ atom first undergoes resonance ionization (RI) in which the excited $2s$ electron tunnels into a vacant level above the Fermi surface. The resulting $\text{He}^+$ ion continues toward the surface where it is neutralized by a conduction electron from the metal. The energy released is communicated to a second electron which, if the energy transfer is sufficient, may be ejected from the surface. This Auger neutralization (AN) process results in a relatively structureless ejected electron energy distribution that reflects, approximately, a self convolution of the local density of electronic states at the surface. At low work function surfaces RI cannot occur because, as illustrated in Fig. 1b, there are no unfilled levels of appropriate energy available. The $2^3S$ atoms are then deexcited by an Auger deexcitation (AD) process in which an electron from the metal tunnels into the $2^3S$ $1s$ core hole. The energy released is communicated to the excited $2s$ electron which may be ejected. Since AD is a quasi-one-electron process, the ejected electron energy distribution reflects directly the local density of electronic states and can contain relatively sharp features. The presence of adsorbed layers on a surface can also impede RI by preventing good overlap between the $2s$ electron wavefunction and vacant levels in the metal. Deexcitation may again occur by AD and, because the electron that tunnels into the $2^3S$ $1s$ core hole originates in the adsorbate layer, the process is analogous to gas-phase Penning ionization (PI) [4] and is frequently termed surface Penning ionization (SPI).

Fig. 1. Schematic diagram of the electron ejection processes that can occur when $\text{He}(2^3S)$ atoms are deexcited at a clean metal surface.
The ejection processes operate can be probed directly by spin labelling. In RI + AN, the electron originates in the surface suggesting that, for non-magnetic surfaces and in the absence of any spin correlations, the ejected electron polarization should be zero. In contrast, in AD it is the (polarized) 2s electron that is liberated and the ejected electron polarization should equal that of the incident 2s atoms. Data obtained at a clean Au(100) surface show that He(2 5S) deexcitation occurs exclusively through RI + AN, but that the electrons involved in the AN process are correlated in spin, and possible reasons for this are discussed. Studies with Xe and NO films adsorbed on cooled (~25 K) Au(100) and Cu(100) substrates, respectively, are also described and suggest that, although, in essence, deexcitation occurs through SPJ, effects associated with the underlying substrate, and interactions involving neighboring atoms in the film, are important.

The present apparatus is shown schematically in Fig. 2, and has been described elsewhere [1, 2]. Briefly, a fraction of the atoms contained in a ground-state helium atom beam formed by a multichannel array is excited to the 2p5S metastable levels by a coaxial electron beam. The 2p5S atoms are removed from the beam by illuminating it with 206 μm radiation from a helium discharge lamp that excites 2S→2P→1S transitions. Charged particles produced by electron impact are removed by a transverse electric field. A weak magnetic field (~0.5 G) applied perpendicular to the beam to establish a well defined quantization axis. Circularly-polarized 2p→2p resonance radiation from a high-power helium lamp incident along the magnetic field direction is used to optically pump the 2S atoms to increase the relative populations in the Ms(Ml) = +1 or -1 magnetic sublevels. The resultant beam polarization, defined as

\[ P = \frac{n_+ - n_-}{n_+ + n_-} \]  

where n+, n-, and n0 are the number of atoms in the Ms(Ml) = +1, 0, and -1 levels, respectively, is measured by a Stern-Gerlach (SG) analyzer and is typically ~0.40. A mechanical chopper is used, in conjunction with time-of-flight techniques, to discriminate against electron ejection caused by photons or fast neutrons that might be produced in the source.

A fraction of the electrons ejected from the target surface enter a retarding-potential energy analyzer that is in series with a compact Mott polarimeter, thereby permitting energy-resolved polarization measurements. The electron polarization is defined by

\[ P = \frac{n_+ - n_-}{n_+ + n_-} \]  

where n+, n-, and n0 are the numbers of electrons with Ms = +1/2 and -1/2, respectively. The apparatus also includes a separate retarding-potential analyzer to enable direct measurements of electron energy distributions (EEDs).

The target surfaces were mounted on a LHe-cooled dewar. They were initially prepared by repeated cycles of 500 eV Ar + sputtering followed by annealing. Surface cleanliness and order were monitored by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), respectively. Sputtering/annealing cycles were continued until surface contamination levels were below the AES detection limit and a sharp LEED pattern was obtained. To prepare adsorbate films, the substrate was cooled to ~20-25 K and the adsorbate gas admitted to the system, typically at pressures of ~10^-6 to 10^-7 torr, until the required exposure was obtained.

The electron energy and polarization distributions observed following He(2 5S) deexcitation at a clean Au(100)
surface are shown in Fig. 3. The electron polarization is expressed as a percentage of that of the 2 Sʰ atoms. (Because atoms in M_s (M_z = 0) states contribute equally to m_s = +1/2 and -1/2 electronic states, consideration of the definitions in (1,2) indicates that the polarization of the electrons on the incident 2 Sʰ atoms is numerically equal to the atom polarization, P_0, and that the polarization of electrons produced in any collision process will be proportional to P_0.) Ejection at a Au(100) surface (d = 5.47 eV) is expected to occur via RI + AN. To check this, EEDs were also measured for incident helium 2 Sʰ and 2 Pʰ atoms and are included in Fig. 3. The 2 Sʰ data were obtained by turning off the quench lamp. The 2 Pʰ atoms were created by transversely illuminating the metastable atom beam at the target surface with 1.06 μm 2 Sʰ → 2 Pʰ, radiation from a single-mode, frequency-stabilized Ti:sapphire laser. Tests revealed that the 300 mW output power provided by the laser was more than sufficient to saturate the 2 Sʰ → 2 Pʰ transition [5]. As evident from Fig. 3, the increased internal energy associated with incident 2 Sʰ and 2 Pʰ atoms does not result in any significant changes in the measured EEDs. The data thus require that ejection occurs exclusively through RI + AN, i.e., in each case the incident atoms are converted to Heʰ ions prior to ejection occurring. This is further confirmed by detailed studies which showed that, for energies above 12 eV, the ejected electron signal changed by less than 1% upon laser illumination.

The observed electron polarization requires that the electrons involved in the AN process tend to have antiparallel spins. This is apparent from Fig. 1a. For incident He(2 Sʰ) atoms with M_z = +1, RI results in the formation of the Heʰ ion whose 1s core hole must be filled by a spin-down electron (the helium ground state is a spin singlet). As shown by experiment, however, this is accompanied by preferential ejection of a spin-up electron, and the formation of singlet two-hole final states at the surface is therefore favored. The measured spin correlation is quite large, especially at the highest ejected electron energies for which both electrons must originate near the Fermi level. This behavior is similar to that noted previously at a Cu(100) surface [5], except that the present correlation is larger, especially at the lower electron energies.

A simple theoretical model has been advanced [6] that explains the earlier Cu(100) observations in terms of interference between direct and exchange Auger processes which diminishes the likelihood of triplet two-hole final states. This model could also account for the present Au(100) results. However, other explanations are possible. Auger transitions can only occur when the Heʰ ion is close to the surface and the presence of the Heʰ ion represents a large perturbation that locally distorts the surface electronic structure, giving rise to many-body effects such as strong charge fluctuations and the Kondo effect [7]. Preliminary calculations suggest that these perturbations might be particularly strong in the case of helium and result in a strong spin dependence in the interaction potential. This spin dependence induces a strongly enhanced local density of spin-up electrons near the Fermi energy. The density of spin-down electrons is reduced slightly. Such a locally-induced spin polarization near the Fermi energy could account for the observed spin correlation and, in particular, its marked increase at the highest ejected electron energies where the electrons involved in the AN process must both originate near the Fermi energy.

Figure 4 shows EEDs observed following 2 Sʰ deexcitation at a cooled Au(100) surface subject to different exposures of Xe. As the surface exposure is increased the total ejected electron signal increases and the broad, relatively featureless distribution characteristic of a clean Au(100) surface evolves into a more structured distribution that, for exposures ≥ 30 L, remains essentially unchanged. The two high-energy features are similar to those observed in gas-phase PI [8], which correspond to ionization into the 3 P_{1/2} and 3 P_{3/2} states of the product Xeʰ⁺ ion, strongly suggesting that they result from SPI. Gas-phase PI of Xe can be described in terms of a direct transition from the covalent He(2 Sʰ)-Xe entrance potential to the final He(1 Sʰ)-Xeʰ⁺ exit potential. Because neither potential is strongly dependent on internuclear separation, ionization via this "covalent" channel results in a narrow distribution of electron energies. The energies of the SPI peaks are, however, significantly higher than observed in gas-phase PI studies indicating that the ionization potential of the Xe atoms on the surface is reduced. This reduction results from a combination of substrate image charge effects and dielectric screening of the product Xeʰ⁺ ion by neighboring Xe atoms [9]. The gradual decrease in the energy of the SPI features with increasing surface exposure reflects the diminution of image charge effects with increasing film thickness. However, even at the highest surface coverages, where image charge effects should be minimal, the energies of the SPI features are ~1.3 eV higher than the corresponding gas-phase PI features. This demonstrates that dielectric screening by neighboring atoms is important, and the size of the energy...
shift is similar to that attributed to dielectric screening in earlier studies of photoemission from adsorbed Xe layers [9].

At high exposures, the electron polarization associated with the high energy features is large and, to within experimental error, is equal to that of the 2S atoms indicating that spin is conserved. Ejection must therefore occur via an AD process in which an electron of appropriate spin from a Xe atom in the adsorbed film tunnels into the He\(2^2S\) 2s core hole with simultaneous ejection of the (polarized) 2s electron, i.e., via the reaction

\[
\text{He}(2^2S)\{n\ell\} + \text{Xe}\{\ell\} \rightarrow \text{He}(1^2S)\{n\ell\} + \text{Xe}^+\{\ell\} + e^-\{\ell\}.
\]

(3)

Since the electron polarization is equal to that of the 2S atoms, which can be simply measured using a SG analyzer, SPI at a Xe film may provide a valuable source of electrons for use in, for example, polarimeter calibration [10].

The measured EEDs, however, also contain a low-energy feature not observed in gas-phase PI with a polarization significantly lower than that of the high-energy feature. To explore further the origin of this feature, EEDs were measured for incident 2S and 2P atoms and are included in Fig. 5. As expected, the energies of the features attributed to SPI increase with the internal energy of the incident atoms. In contrast, the energy of the low-energy feature remains essentially unchanged suggesting that, by analogy to the Au(100) data, it is associated with neutralization of He\(^+\) ions formed by RI. This interpretation is supported by the observed increase in the relative size of the low-energy feature as the internal energy, and RI rate, of the incident atoms increases. Also, because RI forms a polarized He\(^+\) ion, spin correlations might again account for the observed polarization. (Energetically, the low-energy feature is consistent with AN of Xe\(^+\) ions formed by SPI. However, the experimental data do not support this interpretation because comparison of the data obtained with 2S, 2P, and 2P incident atoms shows that the size of the low-energy features does not scale with the size of the SPI features. In addition, although SPI by polarized He(2S) atoms will lead to formation of polarized Xe\(^+\) ions, the polarization of these ions will be rapidly degraded by internal spin-orbit coupling and it is unlikely that AN of Xe\(^+\) ions could lead to ejection of electrons with significant spin polarization.)

It is only possible to speculate as to the process(es) responsible for the low-energy feature. This feature might result from AN of Xe\(^+\) ions through an interaction involving neighboring Xe atoms in which, in essence, two Xe\(^+\) ions are formed. However, the product ions will be created in relatively close proximity and for such a process to be allowed energetically their mutual interaction must be reduced by dielectric screening effects. Although Auger processes that involve neighboring Xe atoms may be slow, He\(^+\) ions formed by RI are bound to the surface by their image charges allowing time for reaction to occur. Alternately, the low-energy feature might involve near-resonant charge transfer between the He\(^+\) ion and a Xe atom in the surface to form an excited Xe\(^{2+}\) ion that undergoes rapid AD accompanied by the ejection of an electron.

The EED observed following He(2S) excitation at an adsorbed NO film is shown in Fig. 6 together with the measured electron polarizations. Also included for comparison is the EED recorded (with higher energy resolution) in studies of gas-phase PI [11] together with corresponding energy-resolved polarizations obtained using a helium flowing afterglow apparatus [12]. The generally good agreement between the gas-phase and surface data suggest that He(2S) excitation again occurs via SPI. The sharp features evident in the gas-phase EED correspond to ionization into the ground \(X^1\Sigma^+\) and excited \(a^3\Sigma^+, b^2\Pi, w^3\Delta\) and \(A^3\Pi\) states of the product NO\(^+\) ion and, as for Xe, are indicative of ionization via the covalent channel. The measured electron polarizations

![Fig. 5. Electron energy distributions resulting from the excitation of He(2S), He(2P) and He(2P) atoms at a Xe film. - - - , ejected electron polarizations measured with polarized He(2S) incident atoms.](image)

![Fig. 6. Comparison of electron energy and polarization distributions measured for surface and gas-phase Penning ionization of NO. Energy distributions: (---) present work; (- - -) gas-phase studies. [11] Polarizations: - - - , present work; o, gas-phase data [12].](image)
are, however, much smaller than for Xe. This can be explained because, unlike Xe, NO is an open shell system which makes possible exchange between the He 2s and NO 2pπ* electrons. If, as the (Mπ = +1) He(2 3S) atom approaches the surface, exchange occurs between the 2s up-spin electron and a down-spin 2pπ* electron subsequent AD will lead to the ejection of a down-spin 2s electron. Although it is not possible to calculate the probability for exchange, it is evident that for open-shell systems SPI need not lead to the production of highly-polarized electrons. Also, NO has a small positive electron affinity and it is possible that reaction might involve a transition from the covalent He(2 3S)-NO entrance potential onto a strongly-attractive He*-NO- ionic potential. Subsequent autoionization of the He*-NO- collision complex can lead to ejection of a down-spin 2pπ* electron from the NO- ion if the product NO+ ion is formed in an excited state [12].

The present data show that spin-labeling techniques provide a novel means to examine the dynamics of He(2 3S) atom desorption at solid surfaces and can reveal correlation and exchange effects not evident from simple analysis of ejected electron energy distributions.

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References
Decay excitation of helium $2^3S$, $2^1S$, and $2^3P$ atoms at Ar and Xe films

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Measurements of ejected electron energy distributions are used in conjunction with electron spin labeling techniques to probe the mechanisms by which He($2^3S$), He($2^1S$), and He($2^3P$) atoms are decayed at Ar and Xe films adsorbed on a cooled Cu(100) substrate. The data for both surfaces contain features similar to those observed in gas-phase Penning ionization, indicating that electron ejection, in part, from Auger decay excitation, i.e., surface Penning ionization. For Xe, however, additional features are observed that can be attributed to resonance ionization of an excited atom followed by neutralization of the resulting He$^+$ ion through an interaction that involves neighboring Xe atoms in the film. Indeed, the Xe data provide an exceptional example of a surface at which Auger decay excitation and resonance ionization occur in parallel with one another, with a branching ratio that changes significantly as the internal energy of the incident atom increases. The ejected electron yield from both Ar and Xe films is substantially higher than that for clean Cu(100), indicating that such films might form the basis of an efficient thermal-energy helium metastable atom detector.

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Interactions of excited atoms with surfaces frequently lead to decay excitation and to electron ejection. Here we present the results of a study of the mechanisms by which He($2^3S$), He($2^1S$), and He($2^3P$) atoms are decayed at Ar and Xe films adsorbed on a clean, cooled Cu(100) surface. The operative processes were investigated by analyzing the energy distribution of the ejected electrons. In the case of He($2^3S$) atoms, additional information was obtained by use of spin labeling techniques—specifically, the use of electron-spin-polarized He($2^3S$) atoms coupled with energy-resolved spin analysis of the product electrons. Conventional models suggest that excited helium atoms will be decayed at clean high-work-function metal surfaces by the two-step process illustrated in Fig. 1(a) [1]. An incident atom first undergoes resonance ionization (RI) in which the excited electron tunnels into a vacant level above the Fermi energy. The resulting He$^+$ ion continues toward the surface where it is neutralized by a conduction electron from the metal. The energy released is communicated to a second electron which, if the energy transfer is sufficient, may be ejected from the surface. This Auger neutralization (AN) process results in a broad relatively structureless ejected electron energy distribution that reflects, approximately, a self-convolution of the local density of electronic states at the surface. The presence of an adsorbate film will, in general, impede RI by preventing good overlap between the excited electron and vacant levels in the metal. The atoms are then decayed by the Auger decay excitation (AD) process diagrammed in Fig. 1(b). An electron from the adsorbate layer tunnels into the vacant 1s core hole, and the energy released is communicated to the excited electron which may be ejected. This process is analogous to gas-phase Penning ionization (PI) [2] and is frequently termed surface Penning ionization (SPI). Since AD is a quasi-one-electron process, the ejected electron distribution will reflect directly the electronic structure of the adsorbate and can contain relatively sharp features. Indeed, SPI has already been used to investigate the electronic properties of a variety of organic materials [3]. AD can also occur at clean metal surfaces of sufficiently low work function that RI is inhibited because there are no unfilled levels of appropriate energy available. In this event, an electron from the metal tunnels into the 1s core hole with simultaneous ejection of the excited electron.

In the case of He($2^1S$) atoms, the operative ejection processes can be probed directly through spin analysis. In RI+AN, the electron originates in the surface, suggesting that, for nonmagnetic surfaces and in the absence of any spin correlations, the ejected electron polarization should be zero. In contrast, in AD (SPI) it is the (polarized) 2s electron that is liberated and the ejected electron polarization should equal that of the incident 2$^1S$ atoms.

Data obtained for helium $2^3S$, $2^1S$, and $2^3P$ atoms incident on Ar and Xe films contain features that can be attributed to AD (SPI) indicating that, in essence, the film

FIG. 1. Schematic diagram of the electron ejection process that occurs when excited helium atoms are decayed at (a) a clean high-work-function metal surface and (b) following deposition of an adsorbate overlayer.

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can behave as a solid gas. The data for Xe, however, contain additional features with no analog in gas-phase Penning ionization that can be ascribed to R1 of incident atoms followed by neutralization of the resulting He* ions through an interaction that involves neighboring atoms in the film. Indeed, the Xe data provide an exceptional example of a surface at which Auger deexcitation and resonance ionization occur in parallel with one another, with a branching ratio that depends on the internal energy of the incident atoms.

The present apparatus is shown schematically in Fig. 2 and has been described in detail elsewhere [4]. Briefly, a fraction of the atoms contained in a ground-state helium atom beam formed by a multichannel array is excited to the 2 $^2S$ metastable levels by a coaxial electron beam. The 2 $^2S$ atoms may be removed from the beam by illuminating it with 2.06 $\mu$m radiation from a helium discharge lamp that excites 2 $^1S$ $\rightarrow$ 2 $^1P$ $\rightarrow$ 1 $^1S$ transitions. Charged particles produced by electron impact are removed by a transverse electric field. A weak (0.5 $G$) magnetic field is applied perpendicular to the beam to establish a well-defined quantization axis. Circularly polarized 2 $^2S$ $\rightarrow$ 2 $^1P$ resonance radiation from a high-power rf-excited helium lamp, incident along the magnetic-field direction, is used to optically pump the 2 $^2S$ atoms to increase the relative populations in the $M_J(M_F)=+1$ or $-1$ magnetic sublevels. The resultant beam polarization $P_b$ is defined as

$$P_b = \frac{n_+ - n_-}{n_+ + n_-},$$  \hspace{1cm} (1)

where $n_+$, $n_-$, and $n_0$ are the numbers of atoms in the $M_J(M_F)=+1$, 0, and $-1$ levels, respectively, as measured by a Stern-Gerlach (SG) analyzer and is typically $\approx 0.45$. A mechanical chopper is used, in conjunction with time-of-flight techniques, to discriminate against electron ejection caused by photons or fast neutral atoms that might be produced in the source. The excited atoms strike the target surface at an angle of incidence $\theta \approx 45^\circ$.

Depending on what measurement is being undertaken, the surface is positioned normal to the axis of either a retarding-potential analyzer or a Mott polarimeter. The retarding-potential energy analyzer [energy resolution = 0.6 eV full width at half maximum (FWHM)] is used to measure ejected electron energy distributions (EED’s). EED’s for the 2 $^2S$ atoms were obtained directly using a pure 2 $^1S$ incident beam. EED’s for 2 $^2S$ atoms were determined by taking the difference between distributions measured with and without the 2 $^1S$ quench lamp turned on. The 2 $^1P$ atoms were created by transversely illuminating the He(2 $^2S$) atom beam at the target surface with 1.08 $\mu$m, 2 $^2S_1$$\rightarrow$2 $^2P_2$ radiation from a single-mode, frequency-stabilized Coherent Model CR899-21 Ti:sapphire laser. Tests showed that the 200 mW output power provided by the laser was more than sufficient to saturate the 2 $^2S$$\rightarrow$2 $^1P$ transition [5], EED’s for 2 $^1P$ atoms were obtained by measuring the distribution for a mixed 2 $^2S$/2 $^1P$ beam and subtracting the 2 $^2S$ contribution. Limited data for Ne(2 $^1S$) metastable atoms were also obtained by admitting Ne to the metastable atom source.

Ejected electron polarizations were determined using a compact Mott polarimeter. This was equipped with a retarding-potential analyzer at its input to permit energy-resolved measurements. The electron polarization $P$ is defined via

$$P = \frac{n_1 - n_{-1}}{n_1 + n_{-1}},$$ \hspace{1cm} (2)

where $n_1$ and $n_{-1}$ are the numbers of electrons with $m_J = \frac{1}{2}$ and $-\frac{1}{2}$, respectively. (Using Eqts. (1) and (2), it can be shown that the net spin polarization of the He(2 $^2S$) atomic electrons is numerically equal to the atomic polarization $P_a$.)

The Cu(100) substrate was mounted on a LHe-cooled Dewar. It was initially prepared by repeated cycles of 500-eV Ar$^+$ sputtering following by annealing. Surface cleanliness and order were monitored by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), respectively. Sputtering-annealing cycles were repeated until surface contamination levels were below the AES detection limit and a sharp LEED pattern was obtained. To produce the adsorbate films, the substrate was cooled to $\approx 30$ K and the adsorbate gas admitted to the system, typically at pressures of $\approx 10^{-6}$ to $10^{-7}$ Torr, until the required exposure was obtained. No well-defined LEED patterns associated with adsorbed Xe or Ar films were observed.

Figures 3(a) and 3(b) show the ejected electron energy distributions observed as a result of He(2 $^2S$) deexcitation at a cooled Cu(100) surface following different exposures to Xe and Ar. (1 L corresponds to an exposure of $10^{-5}$ Torr s, and a exposure of 4 L results in the deposition of approximately one monolayer [6].) The kinetic energy $E_K$ of the ejected electrons is related to the retarding-
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FIG. 3. Electron energy distributions resulting from He(2S) deexcitation at a cooled Cu(100) surface following different exposures to (a) Xe and (b) Ar. Note that the data for clean Cu(100) are multiplied by a factor of 3.

The potential difference $V$ applied between the target and the retarding grid in the energy analyzer by $E_R = eV + \phi_{r} - \phi_{t}$, where $\phi_{r}$ and $\phi_{t}$ are the work functions of the retarding grids and target surface, respectively ($\phi_{t}$ for clean Cu(100) is 4.59 eV [7]). The work function of the retarding grid is, however, not well known, and that of the target surface changes with Xe or Ar exposure [8]. Thus the electron energy scale was fixed, in practice, by positioning the low-energy cutoffs in the EED's at zero energy. For both adsorbates, the integrated ejected electron signals increase as the surface exposure is increased and the broad, relatively featureless distribution characteristic of a clean Cu(100) surface evolves into a more structured distribution which, for exposures $\geq 10^4$ L, remains essentially unchanged. (For surface exposures $\geq 10^4$ L, however, the adsorbed films were sufficiently thick that problems were experienced with surface charging.) The measured EED's remained stable for periods of several hours, indicating that surface contamination by background gas or the helium metastable atom beam was unimportant on the time scale of the present experiments.

The two higher-energy peaks evident in the Xe data are similar to those observed in He(2S) gas-phase PI [9], which correspond to ionization into the $2P_{1/2}$ and $2P_{3/2}$ states of the product Xe$^+$ ion, strongly suggesting that they result from SPI. (The SPI peak associated with ionization into $2P_{1/2}$ states is significantly broader than that for ionization into $2P_{3/2}$ states because, at the surface, the $2P_{3/2}$-like states are removed by interactions with neighboring atoms [10]). Gas-phase PI of Xe can be described in terms of a direct transition from the covalent He(2S)-Xe entrance potential to the final He(1S)+Xe$^+$ exit potential. Because neither potential is strongly dependent on internuclear separation, ionization via this so-called "covalent" channel results in a narrow distribution of electron energies [2]. The separation in energy of the SPI peaks ($\sim 1.3$ eV) is similar to that observed in gas-phase PI, but their absolute energies are significantly higher. This indicates that the binding energy of the atomic $5p^6$ electron is significantly reduced at the surface. This reduction can be attributed to final-state relaxation effects, i.e., to substrate image charges and to dielectric screening of the product Xe$^+$ ion by neighboring Xe atoms, and has been observed in numerous photoemission studies [8]. The gradual decrease in the energy of the high-energy SPI features with increasing Xe exposure is consistent with the decrease in image charge effects expected as the surface coverage increases. However, even at the highest coverages the energies of the SPI features are $\sim 1.3$ eV higher than the corresponding gas-phase PI features. The size of this shift in binding energy is similar to that attributed to dielectric screening in earlier studies of photoemission from adsorbed Xe layers [11].

Gas-phase PI of Ar results in an electron energy distribution that comprises two narrow features separated by $\sim 0.2$ eV that again result from ionization into the $2P_{1/2}$ states of the product ion [9]. Such closely spaced features cannot be resolved in the present apparatus and the single peak observed at high coverages in the Ar EED is therefore consistent with SPI. (Visual inspection of the data in Figs. 3(a) and 3(b), however, shows that the width of the Ar feature is significantly broader than that resulting from SPI of Xe atoms into the $2P_{1/2}$ state.) The energy of the Ar SPI peaks is $\sim 1.1$ eV higher than observed in gas-phase PI, and this shift in binding energy is again consistent with earlier photoemission studies [12].

The ejected electron polarizations associated with the high-energy features in the Xe and Ar EED's at high surface exposures are indicated in Figs. 4(a) and 4(b). (The electron polarization is expressed as a percentage of that of the 2S atoms.) In each case, the electron polarization is large and, to within experimental error, is equal to that of the incident 2S atoms, indicating that spin is conserved. Ejection must therefore occur via an AD process in which an electron of appropriate spin from an atom in the adsorbed film tunnels into the He(2S) 1s core hole with simultaneous ejection of the (polarized) 2s electron, i.e., via the reaction

$$\text{He}(2S) + \text{Xe}(2S) \rightarrow \text{He}(1S) + \text{Xe}^+ + e^-.$$  \hspace{1cm} (3)

(Gas-phase PI of Ar is also observed to occur via such an electron exchange reaction [13]). Because the electron polarization is equal to that of the 2S atoms, which can be accurately measured using a 9G analyzer, SPI at an Ar or Xe film can provide a valuable source of electrons of known polarization for use in, for example, polarimeter calibration [14].

The EED's observed following He(2S) and He(2P) deexcitation at a Xe film are shown, together with that for He(2S), in Fig. 4(a). Similar data for an Ar film are presented in Fig. 4(b). A high-energy feature is evident in each distribution whose energy increases with the internal energy of the incident atoms (19.82, 20.62, and 20.96 eV for the 2S, 2P, and 2P states, respectively), indicating that these features are associated with AD (SPI). The
EED's observed at a Xe film, however, also contain a low-energy feature with no analog in gas-phase PI spectra. The energy of this feature does not depend on the incident species, suggesting that it does not result from AD (SP). In the case of He(2s) atoms, this is further confirmed by the observation that the polarization of the low-energy feature is significantly less [see Fig. 4(a)] than that of the higher-energy features.

Energetically, the low-energy feature is consistent with AN of Xe$^+$ ions formed by SP. The data in Fig. 4(a) suggest that this is not the mechanism responsible for this feature, however, because comparison of the data obtained with 2s, 2p, and 2$^P$ atoms shows that the size of the low-energy feature does not scale with the size of the SP features. Indeed, the data suggest that the low-energy feature grows at the expense of the high-energy feature as the internal energy of the incident atoms increases. EED's were also measured for a Xe film using incident Ne(3P$_{2,3}$) metastable atoms. Two peaks were observed that were consistent with formation of Xe$^+$ ions in 1P$_{1,2}$ states through SP. However, no low-energy feature was evident, further demonstrating that it cannot be attributed to AN of Xe$^+$ ions formed by SP.

To investigate the influence, if any, of the substrate on the low-energy feature, EED's were recorded for thick (~30 L exposure) Xe films adsorbed on clean Au(100) ($\phi_e$ = 5.47 eV [15]) and on a cesiated Cu(100) surface ($\phi_e$ = 2.1 eV [16]). Measurements were also undertaken using Xe films that were isolated from the substrate by an intermediate Ar layer. As illustrated in Fig. 5, no significant substrate dependence of the measured EED's was observed, indicating that the low-energy feature is governed by the properties of the adsorbed film rather than the nature of the substrate.

Because the increased internal energy associated with incident 2s and 2p atoms does not result in any significant change in the profile or position of the low-energy feature, this suggests that it might be associated with neutralization of He$^+$ ions formed through RI, i.e., in each case the incident atoms are converted to He$^+$ ions prior to ejection occurring. RI, however, requires the availability of empty levels at the surface resonant with the excited helium electron. Inverse photoemission studies of adsorbed Xe layers have revealed the presence of unoccupied levels ~1.5 eV below the vacuum level that may be associated with surface states or Xe negative ion states of configuration 5p$^6$6s [17]. (Also, solid Xe has a positive electron affinity, ~0.5 eV [18].) As an excited helium atom approaches the surface, hybridization effects and image charge interactions raise the electronic energy levels relative to the vacuum level [19]. This could move the electronic levels into resonance with unoccupied states in the surface and facilitate RI. This suggestion is consistent with the observed shift in the branching ratio between the low (RI+AN) and high (AD) energy features evident in Fig. 4(a), the size of the low-energy feature growing as the internal energy of the incident atoms, and hence the energy overlap with available empty states at the surface, increases.

![Figure 4](image_url)  
**FIG. 4.** Electron energy distributions resulting from the deexcitation of He(2s), He(2p), and He(2p) atoms at a cooled Cu(100) surface exposed to 30 L of (a) Xe and (b) Ar. The ejected electron polarizations measured with incident polarized He(2s) atoms are also indicated (●). The electron polarization is expressed as a percentage of that of the incident 2s atom.

![Figure 5](image_url)  
**FIG. 5.** Electron energy distributions resulting from He(2s) deexcitation at thick (~30 L exposure) Xe films adsorbed on (a) clean Cu(100), (b) clean Au(100), (c) cesiated Cu(100), and (d) an intermediate Ar layer.
Once a He\(^+\) ion is formed by R1, there are a number of neutralization processes that might give rise to the observed low-energy feature. It might result from an interaction that involves two Xe atoms in the film in which the He\(^+\) ion is neutralized by a 5p electron from one Xe atom tunneling in the He\(^+\) 1s core hole, the energy liberated being used to eject a 3p electron from a neighboring atom. The gas-phase ionization potential of He, 24.58 eV, is more than twice that of Xe, 12.13 eV, suggesting that the process is allowed energetically. However, the product Xe\(^+\) ions must be formed in relatively close proximity (the mean Xe-Xe separation on Cu(100) is \(\sim 4.3 \text{ Å} \)) [20]. Thus, even allowing for dielectric screening effects, their final mutual energy of electrostatic interaction is expected to be significant, perhaps \(\sim 1-2 \text{ eV}\). Nonetheless, the process might still be allowed energetically because perturbations introduced by the surface lower the atomic binding energies and because "cluster" ions such as Xe\(_2\(^+\)) might be formed (the binding energy of Xe\(_2\(^+\)) is \(\sim 1 \text{ eV} \)) [21]). Although Auger processes that involve neighboring Xe atoms may be slow, the kinetic energy of the incident atoms is very low (\(\sim 40 \text{ meV}\)) and He\(^+\) ions formed by R1 may be bound by their image charge, allowing time for reaction to occur. In addition, the He\(^+\) ion that results from R1 of a polarized He(2\(^2\)S) atom is itself spin polarized and spin-correlation effects similar to those recently noted in AN of polarized He\(^+\) ions at a clean metal surface might account for the observed polarization of the low-energy feature [5]. Alternatively, the reaction might proceed via near-resonant charge transfer between the He\(^+\) ion and a Xe atom in the surface to form an excited Xe\(*\(^+\)) ion of configuration 5s5p\(^+\) that undergoes rapid AD through tunneling of a 5p electron from a neighboring Xe atom into the Xe\(*\(^+\)) 5s core hole with simultaneous ejection of a 3p electron from the ion. In the case of polarized He\(^+\) ions, the 5s core hole created by charge transfer is polarized, and spin-correlation effects might again account for the observed polarization.

Assigning the low-energy feature to neutralization of He\(^+\) ions formed by R1 is consistent with the observation that this feature initially grows more rapidly than the high-energy features with increasing exposure to Xe (see Fig. 3). For low surface exposures (coverages) R1 may be enhanced relative to AD (SPI) by the excited electron tunneling directly into the Cu(100) substrate through the adsorbed layer [1]. For thick films, however, direct tunneling is not possible and a balance is established between R1 and AD (SPI).

The present Xe data are noteworthy because they provide an exceptional example of a surface at which R1 and AD (SPI) occur in parallel with one another, with a branching ratio that depends on the internal energy of the incident atoms. At clean, high-work-function metal surfaces where there is a high density of unoccupied levels, electron ejection occurs exclusively through R1+AN [5]. For thick films of many other spin-singlet gases, only AD (SPI) is observed [4]. Two factors may contribute to the balance between R1 and AD (SPI) observed for Xe films. The unoccupied states in the film may be sufficiently close to the vacuum level that the separation between the incident atoms and the surface must become very small before energy resonance is obtained, thereby allowing AD (SPI) to become competitive. Alternatively, the density of unoccupied levels may be sufficiently low as to limit the R1 rate and permit AD (SPI) to compete effectively.

Exposure of a cooled Cu(100) surface to Ar or Xe results in a low-energy feature in the total ejected electron signal. The probability that AN of a low-energy He\(^+\) ion at a clean metal surface will result in ejection of an electron is \(\sim 0.3 \)) [22]. Because deexcitation of helium 2\(^2\)S, 2\(^2\)S and 2\(^2\)P atoms at a clean Cu(100) surface proceeds via R1+AN, it is reasonable to expect that the probability that electron ejection will accompany their deexcitation is also \(\sim 0.3\). The sizeable increase in electron yield observed following Ar or Xe exposure suggests that at Ar or Xe films the probability for electron ejection is \(\sim 0.9\). This large value is, perhaps, not too surprising given the yields measured previously at "chemically cleaned" surfaces [23] and that studies of gas-phase PI of Ar and Xe by helium 2\(^2\)S and 2\(^2\)S atoms show that the angular distribution of the product electrons is asymmetric and is quite strongly peaked in the back direction [24], i.e., in the direction from which the excited atoms are incident. If this is also true for SPI, a majority of the product electrons will be initially directed out of the surface, increasing the probability for electron ejection. In addition, electrons initially directed into the film may be backscattered through elastic collisions with atoms in the film and reemerge, which will further increase the electron yield. (In contrast, electrons entering a metal surface undergo strong inelastic scattering and are unlikely to escape.)

Given the large ejected electron yields from adsorbed Ar or Xe films, they appear attractive for application as an efficient detector of thermal-energy He(2\(^1\)S) metastable atoms.

As discussed previously, the high-energy features observed in the EED's from Ar films result from AD (SPI). This, coupled with the fact that the increases in ejected electron yield that result from deposition of Ar and Xe films are similar, suggests that at Ar films deexcitation results exclusively from AD (SPI). Since no features ascribable to neutralization of He\(^+\) ions are observed in the Ar spectrum, were R1 to occur, it would reduce the total ejected electron signal. This is not unexpected given that, unlike Xe, solid Ar has a negative electron affinity [18].

The present data further demonstrate that measurements of ejected electron energy distributions, coupled with spin labeling techniques, provide a powerful probe of the processes by which excited helium atoms are deexcited at solid surfaces. The techniques can be extended to beams of the heavier rare-gas metastable atoms, allowing study of a wide variety of excited atom-surface interactions.

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Temperature dependence of He(2P_g) reactions: Collision-induced mixing and conversion to He_2(4Pi_s) molecules

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The rate coefficients for mixing between He(2P_g) levels during collisions with ground-state helium atoms and for conversion of He(2P_g) atoms to He_2(4Pi_s) molecules via three-body reactions in helium gas have been investigated over the temperature range 1.6–300 K. The measured rate coefficients for collisionally induced P-state mixing decrease slowly with decreasing temperature, from (1.7±0.3)×10^{-8} cm^3s^{-1} at 300 K to (4.5±0.5)×10^{-10} cm^3s^{-1} at 4.2 K. The rate coefficients for the production of He_2(4Pi_s) molecules via three-body reactions are observed to increase with decreasing temperature and are described by the relation k_π=(2.5+2677 T^{-1})×10^{-32} cm^6s^{-1}. This behavior, which is very different from that noted in earlier studies of the conversion of He(2S_a) atoms to He_2(2Σ^+_g) molecules through three-body reactions, suggests that the reaction is not thermally activated.

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Interactions between atoms in ground and low-lying excited states, and the collisional processes that influence excited-state lifetimes in helium gas have been the subjects of numerous investigations over many years. In particular, relatively large populations (≥10^{10} cm^{-3}) of helium atoms in the 2Σ_a state can easily be produced, and their collisional properties have been extensively studied [1–13]. The He(2Σ_a)+He(1Σ_g) interaction potential is very unusual in that the competition between the He_2(1Σ_g) and He(1Σ_g) core attraction and the He(1Σ_g) exchange repulsion gives rise to a sizable (∼60 meV) repulsive barrier at intermediate nuclear separations (∼3 Å) before yielding to the strongly attractive He_2(2Σ_g^-) potential well at smaller distances (∼1 Å) [1],[10–13]. The presence of this repulsive barrier has been shown to affect dramatically the temperature dependence of He(2Σ_a) diffusion in helium gas [8] and the rate for metastability exchange in He(2Σ_a)+He(1Σ_g) collisions [5–7], and is also responsible for the formation of stable microscopic voids ("bubbles") surrounding He(2Σ_a) atoms in liquid helium [14,15]. The existence of a barrier also means that the conversion of He(2Σ_a) atoms to He_2(2Σ_g^-) molecules via three-body reaction,

He(2Σ_a)+2He(1Σ_g)→He_2(2Σ_g^-)+He(1Σ_g),

must be thermally activated. Surprisingly, recent experiments in this laboratory have revealed that the effective activation energy decreases at low temperatures, suggesting that, for certain reaction geometries, the barrier can be significantly lowered by the presence of the third body [16].

In this paper we report measurements of the temperature dependence of the rate coefficients for mixing between different He(2P_g,2P_f) sublevels in collisions with ground-state helium atoms via the reaction,

He(2P_g)+He→He(2P_f)+He .

Knowledge of collisional mixing rates is important in the interpretation and further development of He(2Σ_a) optical pumping techniques for producing spin-polarized electron beam targets [17] and spin-polarized ^3He targets for nuclear scattering experiments [18], and for studies of low-temperature ^3He and ^4He quantum fluids [19]. In addition, we have investigated the temperature dependence for conversion of He(2P_g) atoms to He_2(4Pi_s) molecules through three-body reactions in helium gas of the type

He(2P_g)+2He(1Σ_g)→He_2(4Pi_s)+He(1Σ_g).

Reactions (1) and (3) are among the simplest of all ternary reactions and are amenable to investigation over an extraordinarily wide range of temperatures. Thus a thorough study of these systems promises new insights regarding ternary reaction dynamics. Further, spectroscopic studies of He(2P_g) atoms in liquid helium suggest that, like He(2Σ_a) atoms, they repel the ground-state fluid and are surrounded by a nonspherical "bubble" that approximately mirrors the probability density of the 2p orbital [15]. This would imply the existence of a repulsive barrier in the He(2P_g)+He(1Σ_g) interaction potential at intermediate nuclear separations, as for the He(2Σ_g^-)+He(1Σ_g) interaction. However, the exchange repulsion, and thus interaction potential, should depend strongly on the collision geometry, being smallest when the internuclear axis is in the nodal plane of the 2p orbital where the p-electron probability density is a minimum. The present data show that reaction (3) does not require thermal activation, indicating that, at least for collisions near the 2p nodal plane, exchange repulsion is insufficient to produce a barrier.

Studies of reactions involving He(2P_g) atoms, which
are typically produced by photoexcitation of He(2 \, S_1) atoms, have been hampered by the lack of a convenient tunable source of monochromatic radiation at the wavelengths (\sim 1.083 \, \mu m) required for exciting 2 \, S_1 \rightarrow 2 \, P_1 transitions, and by the short radiative lifetime (\sim 10^{-7} \, \text{s}) of the 2 \, P_1 states, which limits attainable He(2 \, P_1) densities. In the present work, rate constants for \( P \)-state mixing [reaction (2)] were derived through line-shape analysis from measurements, undertaken using a Ti:sapphire laser, of the absorption profiles for 2 \, S_1 \rightarrow 2 \, P_0, 2 \, P_2 transitions in a weak rf discharge in helium gas. Rate constants for three-body conversion [reaction (3)] were obtained by using the laser to partially saturate a particular 2 \, S_1 \rightarrow 2 \, P_2 transition and monitoring the decay of the resulting radiation-coupled 2 \, S_1, 2 \, P_2 populations in the afterglow of a pulsed rf discharge.

The present apparatus is shown schematically in Fig. 1. Its central component is a cylindrical Pyrex sample cell that was initially prepared by baking and electrical-discharge cleaning and then filled with helium gas to the desired density. For measurements at low temperatures the cell was immersed in either liquid nitrogen or liquid helium, and temperatures below the 4.2-K liquid-helium boiling point at atmospheric pressure were achieved by pumping the vapor to reduce its pressure. Helium atoms in the cell were excited to the 2 \, S_1 state by igniting a weak electrodeless 3-MHz rf discharge. Care was taken to ensure that the rf discharge power was low enough to avoid heating the sample gas significantly.

Line shapes for the 2 \, S_1 \rightarrow 2 \, P_2 transitions were measured using a single-mode, frequency-stabilized Coherent CR899-21 Ti:sapphire laser, which was optimized for operation at 1.083 \, \mu m, by scanning the laser output frequency and recording the corresponding absorption spectrum. The expected line shape is a convolution of a Gaussian resulting from Doppler (inhomogeneous) broadening,

\[
\frac{\Delta \omega_p}{c} = 2 \Delta \omega_p \left( \frac{2 \lambda T \ln 2}{M} \right)^{1/2},
\]

(5)

and a Lorentzian \( g_L(\omega, \omega_0) \) representing homogeneous broadening due to spontaneous emission and collisional \( P \)-state mixing,

\[
g_L(\omega, \omega_0) = \frac{\Delta \omega_p}{\pi} \frac{\Delta \omega_p}{(\omega_0 - \omega)^2 + (\Delta \omega_p/2)^2},
\]

(6)

with linewidth

\[
\Delta \omega_p = 2 (A + k_n N) = 2 (A + \sigma_m b N),
\]

(7)

where \( \omega_0 \) is the transition frequency at line center, \( \omega \) the laser frequency, \( k_n \) the Boltzmann constant, \( T \) the absolute temperature, \( M \) the helium mass, \( c \) the velocity of light, \( A \) the spontaneous emission rate, \( N \) the helium number density, \( b \) the mean relative collision velocity, and \( \sigma_m \) the rate coefficient and thermally averaged cross section, respectively, for collisional mixing.

The measured line shape, represented by the convolution integral

\[
g_c(\omega, \omega_0) = \int_\infty^{-\infty} g_L(\omega, \Omega) g_L(\Omega, \omega_0) d\Omega
\]

(8)

and commonly called the Voigt function, is easily decomposed by a simple graphical analysis procedure to yield the widths \( \Delta \omega_c \) and \( \Delta \omega_p \) of the Gaussian and Lorentzian components [20,21]. The rate coefficients and thermally averaged cross sections are obtained from the extracted values of \( \Delta \omega_p \) using Eq. (7).

Absorption profiles for He(2 \, S_1) \rightarrow He(2 \, P_2) transitions were measured at temperatures of 300, 77, and 4.2 K, for sample gas densities in the range \( \sim 10^{-7} \, \text{cm}^{-3} \) to \( \sim 5 \times 10^{11} \, \text{cm}^{-3} \). The intensity of the rf discharge was adjusted to the lowest sustainable level to avoid significant heating and to ensure that the absorption profiles were measured using optically-thin samples. The absorption at line center was typically \sim 10%. Laser frequency drift during absorption scans, however, can distort the measured profiles, and changes in laser intensity can cause baseline drift. An absorption profile was deemed acceptable only if it exhibited little or no baseline drift, if upon analysis it yielded a Gaussian linewidth component \( \Delta \omega_c \) within 10% of that calculated using Eq. (5), and if the values of \( \Delta \omega_L \) and \( \Delta \omega_p \) extracted from near-wing and far-wing portions of the spectrum agreed to within 15%.

A typical 2 \, S_1 \rightarrow 2 \, P_2 absorption profile, obtained at a temperature of 4.2 K and gas density of \( 1.25 \times 10^{18} \, \text{cm}^{-3} \), is shown in Fig. 2. Values of \( k_n \) and \( \sigma_m \) obtained from such data are presented in Table I. The uncertainties are estimated to be \frac{\pm 25\%}{\text{at 300 and 77 K}, and} \frac{\pm 10\%}{\text{at 4.2 K}}.

The rate coefficient for \( P \)-state mixing decreases slowly with decreasing temperature, and the cross sections are consistent with the \( T^{-1/3} \) dependence predicted by Langevin "spiralizing-orbit" theory for an \( s^{-6} \) interaction potential, superimposed on a hard-sphere cross section of about \( 6 \times 10^{-12} \, \text{cm}^2 \) [22]. The cross section measured at
TABLE I. Measured rate coefficients and thermally averaged cross sections for $P$ state mixing, reaction (2).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_p$ (10^{-18} cm^3 s^{-1})</th>
<th>$\sigma_p$ (10^{-28} cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>18.5</td>
<td>2.06</td>
</tr>
<tr>
<td>77</td>
<td>12.3</td>
<td>1.04</td>
</tr>
<tr>
<td>4.2</td>
<td>4.5</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*Reference [23].

300 K is in satisfactory agreement with the value (68.23 x 10^{-18} cm^3 s^{-1}) reported previously by Schearer [23].

To obtain rate constants for three-body conversion, reaction (3), the laser was tuned to the center of one of the $2^3 S_1 - 2^3 P_2$ transitions and the decay of the radiation-coupled $2^3 S_1 / 2^3 P_2$ population in the late afterglow of a pulsed rf discharge was measured by observing the time dependence of the absorption of the laser radiation. The discharge was excited by low-power rf pulses of ~100-μs duration with a pulse repetition frequency between 10 and 150 Hz depending on sample density and temperature. The use of low-power pulses assured that the fractional absorption of the laser-probing radiation during the period over which data were recorded was small: ≤ 5% for $T \geq 200$ K and ≤ 2% at lower temperatures.

In our earlier study of the temperature dependence for conversion of He(2 $^3 S$) metastable atoms to He$_2$($^3 S_1$) molecules, it was demonstrated that at high helium densities diffusion can be neglected and that in the late afterglow the only significant He(2 $^3 S$) loss mechanism was three-body conversion, reaction (1) [16]. The He(2 $^3 S$) concentration during the time interval over which data were recorded was well described by the relation

$$\frac{d\Sigma}{dt} = -k_p N S,$$

where $\Sigma$ and $N$ are the densities of metastable $2^3 S_1$ and ground-state $^3 S_0$ helium atoms respectively, and $k_p$ is the rate constant for reaction (1). The He(2 $^3 S_1$) volume loss rate, $\alpha = k_p N S$, was determined by monitoring the absorption of $2^3 S_1 - 2^3 P_2$ resonance radiation from a conventional helium discharge lamp.

Atoms excited to $2^3 P_2$ levels by the probing radiation returned to the $2^3 S_1$ state by spontaneous emission with lifetime $\sim 10^{-3}$ s. The intensity provided by the lamp was sufficiently low that the fraction of the excited atoms in $2^3 P_2$ levels at any instant was less than $10^{-6}$ and their collisions thus provided a negligible contribution to the measured He(2 $^3 S_1$) loss rate.

The Ti:sapphire laser can produce much higher fractional $2^3 P_2$ populations and their collisions become important. As demonstrated by the simple kinetic model presented in the Appendix, measurements of the volume decay rate of the radiation-coupled $2^3 S_1 / 2^3 P_2$ population in the late afterglow as a function of laser intensity and gas density can yield the rate coefficient $k_p(T)$ for three-body conversion, reaction (3). Tests verified that the excited atom population decayed exponentially and that the measured decay rate was independent of the rf pulse power. The laser radiation uniformly illuminated the entire sample cell to minimize possible effects associated with local variations in He(2 $^3 S_1$) density.

The only significant processes for destruction of He(2 $^3 S_1$) and He(2 $^3 P_2$) atoms in the late afterglow are reactions (1) and (3), and diffusion to the container walls. As shown in the Appendix, the common volume decay rate $\alpha$ of the radiation-coupled states is given by

$$\alpha = \frac{(A + R)}{[1 + \frac{g_p}{g_S}]} \left[ k_p N^2 + \frac{D_S}{\lambda N} \right] + \frac{g_p}{g_S} \left[ k_p N^2 + \frac{D_p}{\lambda N} \right].$$

where $g_S$ and $g_p$ are the statistical weights of the two coupled states, $D_S$ and $D_p$ are the diffusion coefficients of He(2 $^3 S_1$) and He(2 $^3 P_2$) atoms normalized to unit helium gas number density, $\lambda$ is the lowest mode diffusion length of the sample cell, and $R$ is the stimulated emission rate given by

$$R(\omega) = \frac{1}{8\pi} A g_p(\omega, \omega_0) I(\omega) \eta_{\omega_0}.$$
\[
\frac{da}{dl(\omega_0)} = \frac{\gamma_{ij}^2}{\gamma_{2s}^0 \omega_0^2} \epsilon(\omega_0, \omega_0) \times \left( (k_F - k_S)^2 \bar{N}^2 + \frac{(D_F - D_S)}{\bar{N}^2} \right) .
\] (12)

Typical data showing the dependence of the measured decay rates \( \alpha \) on laser intensity \( I(\omega_0) \) are presented in Fig. 3. These data were obtained with the laser tuned to the \( ^2S_1 \to ^2P_3 \) transition at a fixed helium sample density \( N = 3.23 \times 10^{10} \) cm\(^{-3} \) for several different sample temperatures in the liquid-helium range. The slopes \( da/dl(\omega_0) \) are seen to be strongly dependent on sample temperature. As expected, the measured slopes were five times smaller with the laser tuned to the \( ^2S_1 \to ^2P_1 \) transition \( (g_{P_1} = 5) \). The small nonzero intercept in Fig. 3 is due to He\(^2(\ ^2S_1) \) losses by diffusion to the walls of the sample cell. [See Appendix, Eq. (A10). The rate coefficient \( k_S \) is negligibly small at liquid-helium temperatures.]

Values of \( da/dl(\omega_0) \) measured over a wide range of helium densities and temperatures revealed no evidence of significant contributions from the diffusion term \( (D_F - D_S)/\bar{N}^2 \) in Eq. (12). Indeed, at all temperatures \( da/dl(\omega_0) \) was found to be simply proportional to \( N g_{2s}(\omega_0, \omega_0) \). This is illustrated in Fig. 4 where the density dependence of \( da/dl(\omega_0) \) is plotted at 77 and 300 K. The shaded regions are proportional to \( N^2 g_{2s}(\omega_0, \omega_0) \), and encompass the uncertainties in \( g(\omega_0, \omega_0) \) that result from uncertainties in the measured values of \( \kappa_{2s} \). [The procedure employed to calculate the density and temperature dependence of \( g_{2s}(\omega_0, \omega_0) \) is described in the Appendix and representative values of \( g(\omega_0, \omega_0) \) for the present experimental conditions can be obtained using Table I.] For comparison, the dashed line in Fig. 4 shows a simple \( N^3 \) dependence. Because the diffusion term in Eq. (12) is negligible, the measured slopes \( da/dl(\omega_0) \) are directly related to \( (k_F - k_S) \), i.e., \( k_F \) since \( k_F < k_S \).

The measured reaction rate coefficients \( k_R(T) \) are presented in Fig. 5. These depend linearly on \( T^{-1} \) and are accurately represented by the function

\[
k_R(T) = (2.5 + 267 T^{-1}) \times 10^{-32} \text{ cm}^6 \text{s}^{-1} ,
\] (13)

shown as the solid line in Fig. 5. The observed \( T^{-1} \) dependence is consistent with the predictions of a simple model based on detailed balancing and kinetic theory developed earlier by Niles and Robertson [24] to explain their experiments which showed that the rate coefficient for conversion of He\(^+ \) ions to molecular He\(_2\)\(^+ \) ions via the three-body reaction

\[
\text{He}^+ + 2\text{He}(\ ^1S_0) \rightarrow \text{He}_2^+ + \text{He}(\ ^1S_0)
\] (14)
also varies at $T^{-1}$.

The magnitude and temperature dependence of $k_s$ is in marked contrast to that of $k_2$, the corresponding rate coefficient for reaction (1), reproduced in Fig. 6 [16]. While reaction (3) is clearly exothermic, the rapid decrease in $k_s$ with decreasing temperature shows that reaction (1) is thermally activated. The temperature-dependence of $k_s$ is well represented by the function

$$k_s(T) = T \left( 8.7 \exp(-750/T) + 0.41 \exp(-200/T) \right) \times 10^{-36} \text{ cm}^6 \text{ s}^{-1},$$

(15)

shown as the solid line in Fig. 6 [16]. The first term, which dominates at high temperatures, corresponds to an activation energy $750 \pm 70$ K (6444 eV) equal (as expected) to the known height of the He(2$^1$S$_0$)–He(1$^1$S$_0$) repulsive barrier [10–13]. However, at lower temperatures $k_s$ is much greater than expected, suggesting that for certain reaction geometries the barrier height along the He(2$^2$S$_1$)–He(1$^1$S$_0$) reaction path is significantly reduced by the presence of the second He(1$^1$S$_0$) atom [16]. This is reflected in the second term in Eq. (15), which suggests that at low temperatures the reaction can be adequately characterized by an effective (or average) activation energy of 200±20 K (1742 eV). It is interesting that, while $k_s$ varies at $T^{-1}$, the prefactor in Eq. (15) for $k_s$ is $T$. This was demonstrated by measurements showing that values of $k_s$ for the light He isotope are $\pm 33\%$ higher than those for He, reflecting the higher thermal velocity of the lighter isotope [16].

The observation that reaction (3) is exothermic can be reconciled with earlier studies suggesting that He(2$^3$P$^1$) atoms tend to repel ground-state atoms in liquid helium by remembering that the He(2$^2$P$^1$)–He(1$^1$S$_0$) exchange repulsion will be small for collisions in which the internuclear axis is in the nodal plane of the 2p-electron orbital, and is apparently insufficient to produce a significant potential barrier [14,15]. Thus, in order for reaction (3) to proceed, it would seem necessary that at least one of the two He(1$^1$S$_0$) atoms approaches the He(2$^3$P$^1$) atom (or close to) the 2p nodal plane.

Reactions (1) and (3) are among the most fundamental three-body reactions that can be studied in the laboratory over an extended temperature range. Theoretical efforts to determine the pertinent potential-energy surfaces would enable molecular dynamics calculations for quantitative comparisons with the results presented here and in Ref. [16].

The authors are grateful to N. F. Lane for valuable discussions regarding helium interaction potentials and bubble states of He(2$^2$S$_1$) and He(2$^3$P$^1$) atoms in liquid helium. This research is supported by National Science Foundation Grant No. PHY-9021196 and by the Robert A. Welch Foundation.

**APPENDIX: BEHAVIOR OF A RADIATIVELY-COUPLED 2$^1$S$_0$ → 2$^3$P$_0$ POPULATION**

The Ti:sapphire laser excites transitions between the helium 2$^1$S$_0$ level and one of the 2$^3$P$_0$ levels shown in the partial term diagram Fig. 7 [25], and is also used to monitor, through absorption, their combined populations in the afterglow of a pulsed rf discharge. In the early afterglow, immediately following the rf pulse, significant production of He(2$^1$S$_0$) atoms can occur as the result of the He(2$^1$S$_0$) atom to He(2$^1$S$_0$) conversion in superelastic collisions with electrons. An important loss channel is Penning ionization in collisions between pairs of excited atoms that results in ionization of one and deexcitation of the other. Both these processes can be neglected in the late afterglow where He(2$^1$S$_0$) to He(2$^3$S$_1$) conversion is essentially complete and the excited atom density is low [3,4,16]. Thus, a simple two-level model can provide an adequate description of the time evolution of the optically coupled 2$^1$S$_0$→2$^3$P$_0$ population in the late afterglow, provided that the radiation field is sufficiently weak that the 2$^3$P$_0$→2$^3$S$_1$ spontaneous emission rate is much greater than that for stimulated emission. The He(2$^1$S$_0$) and He(2$^3$P$_0$) production and loss mechanisms, and their associated rates, are as indicated in Fig. 8. The symbols

![FIG. 6. Rate coefficient $k_s(T)$ for reaction (1) as a function of $1/T$. ○, experimental data; ——, Eq. (15).](image)

![FIG. 7. Partial term diagram showing the levels of interest in this work.](image)
used in the figure and the following text are defined as follows: $N$, number density of ground-state He(1 $^1S_0$) atoms; $S,P$, number densities of He(2 $^2S_1$) and He(2 $^2P_J$), atoms; $g_S,g_P$, statistical weights of the 2 $^2S_1$ and 2 $^2P_J$ states; $D_S,D_P$, diffusion coefficients for He(2 $^2S_1$) and He(2 $^2P_J$) atoms normalized to unit helium number density; $A$, lowest mode diffusion length of the sample cell; $k_x,k_y$, rate coefficients for three-body conversion, i.e. re- actions (1) and (3); $\omega$, laser frequency; $\omega_0,\lambda_0$, transition frequency and wavelength; $I(\omega)$, intensity of radiation field at frequency $\omega$; $A$, He(2 $^2P_J$) spontaneous emission rate, $=10^7$ s$^{-1}$; $R$, He(2 $^2P_J$) stimulated emission rate; and $g_s(\omega_0,\omega_0)$, absorption (Voigt) line-shape function [Eq. (8)].

The differential equations that govern the decay of the $^2S_1$ and $^2P_J$ populations in the late afterglow are

$$\frac{dS}{dt} = - \left( \frac{g_P}{g_S} + \frac{D_S}{N \lambda^2} + k_x N^2 \right) S + (R + A) P \quad \text{(A1)}$$

$$\frac{dP}{dt} = \frac{g_P}{g_S} S - \left( R + A + \frac{D_P}{N \lambda^2} + k_y N^2 \right) P \quad \text{(A2)}$$

These coupled equations have solutions of the form $S,P e^{-\alpha_t}$ and yield two rate coefficients. The first,

$$\alpha_t = A + R \left[ 1 + \frac{g_P}{g_S} \right] \geq 10^5 \text{ s}^{-1}, \quad \text{(A3)}$$

characterizes the rate at which the $S$ and $P$ populations equilibrate with one another in the presence of the radiation field. The second,

$$\alpha = \frac{k_y N^2 + \frac{D_P}{\Lambda^2 N} + \frac{R + A}{g_S} \frac{k_x N^2 + \frac{D_P}{\Lambda^2 N}}{A + R \left[ 1 + \frac{g_P}{g_S} \right]}}{A + R} \leq 10^5 \text{ s}^{-1}, \quad \text{(A4)}$$

is simply the decay rate of the coupled $^2S_1/^2P_J$ population that is measured in the experiment. Because $\alpha \ll \alpha_t$, the $^2S_1$ and $^2P_J$ populations are in quasiequilibrium with one another and the ratio of their densities is

$$P = \frac{\frac{S}{R}}{S} \left[ 1 + \frac{A}{R} \right]^{-1}. \quad \text{(A5)}$$

In the limit $R \gg A$, $P/S = g_P/g_S$ and

$$\alpha = \frac{k_y N^2 + \frac{D_S}{\Lambda^2 N} + \frac{R + A}{g_S + g_P} \frac{k_x N^2 + \frac{D_P}{\Lambda^2 N}}{A + R}}{A + R} \quad \text{(A6)}$$

is simply a weighted linear combination of the $^2S_1$ and $^2P_J$ decay rates. The two-level model developed here is, however, inadequate for interpreting experiments that utilize intense radiation fields because it does not take into account $P$-state mixing which transfers laser-excited $^2P_J$ atoms to other $^2P_J$ levels that can only decay by spontaneous emission. However, in the limit $R \ll A$, $P/S = g_P/g_S$ and $A$, so $S \gg P$ and $\alpha$ is given to a good approximation by

$$\alpha = \left[ \frac{k_y N^2 + \frac{D_S}{\Lambda^2 N}}{A} \right] + \frac{R + A}{g_S} \left[ (k_y - k_x) N^2 + \frac{(D_P - D_S)}{\Lambda^2 N} \right] \frac{R}{A} \quad \text{(A7)}$$

If the laser is tuned to the center of a particular $^2S_1-^2P_J$ transition, the stimulated emission rate is given by

$$R = \frac{\lambda^2}{8\pi} g_s(\omega_0,\omega_0) I(\omega_0) \frac{\lambda^2}{8\pi} g_s(\omega_0,\omega_0) \times \left[ (k_y - k_x) N^2 + \frac{(D_P - D_S)}{\Lambda^2 N} \right] \quad \text{(A8)}$$

and the decay rate $\alpha$ is related to the intensity of the exciting radiation by

$$\frac{da}{dI(\omega_0)} = \frac{g_P}{g_S} \frac{\lambda^2}{8\pi} g_s(\omega_0,\omega_0) \times \left[ (k_y - k_x) N^2 + \frac{(D_P - D_S)}{\Lambda^2 N} \right] \quad \text{(A9)}$$

If no laser radiation is present, $I(\omega_0) = 0$ and $\alpha$ is given by

$$\alpha(I = 0) = k_y N^2 + \frac{D_S}{\Lambda^2 N}, \quad \text{(A10)}$$

which is simply the decay rate appropriate to a pure 2 $^2S_1$ population. The two-level model is adequate in the
TABLE II. Representative values of $\text{Re} [Z(\xi)] = (\Delta \omega_G / 0.935)^{\frac{1}{2}} (\omega_a, \omega_b)$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$N$ ($10^{18}$ atoms cm$^{-3}$)</th>
<th>$\Delta \omega_G$ (cm$^{-1}$)</th>
<th>$\Delta \omega_G$ (cm$^{-1}$)</th>
<th>$\text{Re} [Z(\xi)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>292</td>
<td>50</td>
<td>10.6</td>
<td>1.8</td>
<td>0.864±0.03</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>3.6</td>
<td>0.75±0.05</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>5.4</td>
<td>0.66±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td>0.59±0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>25</td>
<td>5.44</td>
<td>0.62</td>
<td>0.90±0.03</td>
</tr>
<tr>
<td>50</td>
<td>1.2</td>
<td>0.82±0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>1.8</td>
<td>0.75±0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>2.4</td>
<td>0.69±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>3.0</td>
<td>0.64±0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>15</td>
<td>1.27</td>
<td>0.16</td>
<td>0.89±0.01</td>
</tr>
<tr>
<td>30</td>
<td>0.29</td>
<td>0.82±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>15</td>
<td>0.98</td>
<td>0.14</td>
<td>0.88±0.01</td>
</tr>
<tr>
<td>30</td>
<td>0.26</td>
<td>0.79±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>15</td>
<td>0.79</td>
<td>0.13</td>
<td>0.86±0.02</td>
</tr>
<tr>
<td>30</td>
<td>0.24</td>
<td>0.77±0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated from Eq. (7) using Table I. Values of $k_r$ at 2.5 and 1.6 K are estimated from the relation $\sigma_n = [5.8 \pm 2.1 \times 10^{-11}] \times 10^{-11}$ cm$^2$, which fits the data in Table I and is consistent with Langevin theory. Estimated uncertainties are ±25% at 292 and 77 K, ±10% at 4.2 K and below. Reference [26].

$R << A$ limit because the great majority of the excited $2^3P_1$ atoms return to the $2^3S_1$ state via spontaneous emission with rate $A$, which is common to all three $J$ levels. Thus collisional mixing is of little consequence to the kinetics.

To extract rate constants for three-body conversion from measured decay rates $\alpha$, it is necessary to evaluate the integral in Eq. (8) for the Voigt line-shape function, which depends on both temperature and the gas density because of collisional mixing. However, the line-shape function can be determined using the known rate constants $k_r$ for collisional mixing and the integral evaluated in terms of the tabulated form [26]

$$Z(\xi) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}/t}{\xi - t} \, dt, \text{ Im}Z > 0,$$  \hspace{0.5cm} (A11)

where

$$\xi = 1.665 \frac{\Delta \omega_L - \omega}{\Delta \omega_G} + i \left[ 0.833 \frac{\Delta \omega_L}{\Delta \omega_G} \right],$$  \hspace{0.5cm} (A12)

by reexpressing Eq. (8) in complex form as

$$g(\omega_a, \omega_b) = \text{Im} [\tilde{g}(\omega_a, \omega_b)]$$

$$= \text{Im} \left[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{g}_L(\omega, \Omega) \gamma(\Omega, \omega_a, \omega_b) d\Omega \right],$$  \hspace{0.5cm} (A13)

where

$$\tilde{g}_L(\omega, \Omega) = \frac{1}{\pi} \frac{1}{(\Omega - \omega) + i \frac{\Delta \omega_L}{2}},$$  \hspace{0.5cm} (A14)

is the complex Lorentzian. For $\omega = \omega_0$

$$\tilde{g}_L(\omega_0, \omega_0) = \frac{0.935}{\Delta \omega_G} \text{Re} [Z(\xi)].$$  \hspace{0.5cm} (A15)

Representative values of $\text{Re} [Z(\xi)]$ appropriate to the experimental analysis are presented in Table II.

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