Surface Ionization of Metastable Calcium Atoms

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We report an experimental study of surface ionization of metastable calcium atoms on a hot polycrystalline tungsten surface in vacuum. We implemented a hollow-cathode discharge to excite a fraction of calcium atoms in an atomic beam to metastable states and collected the resulting calcium ions. We observed that metastable calcium atoms are ionized with a significantly greater efficiency than ground-state atoms, and the results suggest that virtually every metastable atom impacting the hot surface is ionized. These results demonstrate the potential of metastable atom surface ionization as a means of enriching calcium isotopes for applications in medicine, metrology, and fundamental science.

I. INTRODUCTION

When atoms with ionization energy \( I \) are adsorbed on a metal surface with electronic work function \( \Phi \), the degree of ionization of the atom, \( \alpha \), is given by the Saha-Langmuir equation:

\[
\alpha = \frac{n_i}{n_0} = \frac{g_i e^{(-I - \Phi)/k_B T}}{g_0},
\]

(1)

where \( n_i \) is the flux of surface ions emitted from the surface, \( n_0 \) is the flux of desorbed neutrals, \( g_0 \) and \( g_i \) are the statistical weights of the atomic and first ionic ground states, respectively, and \( T \) is the temperature of the heated metal surface. Should the surface work function be comparable to or exceed \( I \), a significant fraction of the incident neutral atoms will evaporate from the surface as ions. The efficiency of surface ionization is given by \( \beta = \alpha/(1 + \alpha) \) and is defined as the ratio of ions emitted from the surface to the total flux of atoms incident on the surface.\(^2,3\)

The theoretical and experimental aspects of surface ionization have been thoroughly documented\(^4-8\) and this phenomenon has been implemented as a detection tool for atomic beams,\(^2\) as an ion source,\(^9,10\) and as a means of determining the ionization energy of exotic elements.\(^11,12\) Since the work function of refractory metals is no greater than \( \sim 6 \text{ eV} \), surface ionization has largely been limited to the alkali elements. In this article, we report results on the surface ionization of metastable calcium atoms on a polycrystalline tungsten surface. We demonstrate that metastable atoms undergo surface ionization with a greater efficiency than ground-state atoms. Metastable atoms can be selectively surface ionized with an appropriately selected electronic work function if \( I_{ex} < \Phi < I_{gs} \), where \( I_{ex} \) is the ionization energy of the metastable state and \( I_{gs} \) is the ionization energy of the ground state. In alkaline earth and alkaline earth-like systems, this phenomenon has a direct application in atomic clocks, wherein a single frequency-stabilized laser is used to pump a narrow clock transition and the selective surface ionization of the resultant metastable atoms may yield a markedly higher signal-to-noise ratio than conventional atomic clock configurations.\(^13\)

Furthermore, the ability to selectively ionize excited atoms on a metal surface can be exploited for isotope-selective detection and isotope enrichment: atoms of the desired isotope may be optically pumped by a resonant laser to an excited state. With an appropriately selected metal surface, the surface ionization efficiency may be significantly higher for the excited atoms.\(^14,15\)

Such an approach to enable the surface ionization of metastable atoms has the potential to be developed into a means of enriching specific calcium isotopes. The benefits of this approach are readily apparent in medicine, where calcium isotopes are routinely used to diagnose calcium absorption and metabolism disorders.\(^16,17\) Furthermore, when selectively exciting individual isotopes to metastable states, our approach may be used in conjunction with an ion optics system to extract, collect, and thereby enrich atoms of the desired isotope. Calcium compounds enriched with Ca-48 have a number of applications in fundamental science pertaining to the detection of neutrinoless double-beta decay.\(^18,19\)

II. EXPERIMENTAL SETUP

A schematic diagram of the setup is shown in Fig. 1. Calcium granules are vaporized in a capillary oven and a fraction of the atoms in the resulting beam are excited to the metastable \( 4s4p^3P_J \) triplet in a glow discharge.\(^20,21\) A pair of transverse parallel plates about 15 cm downstream from the discharge is used to extract all charged particles remaining in the beam. The atomic beam subsequently impinges on a surface ionization apparatus (SIA) consisting of a polycrystalline tungsten wire as the ionizing surface and a surrounding stainless steel ion detector. The oven and tungsten wire within the SIA are operated at temperatures not exceeding 650°C and 1750°C, respectively. The pressure in the vacuum chamber, as monitored by two gauges, was on the order of \( 10^{-7} \text{ Torr} \) after stabilizing for several hours. At this pressure, there was a persistent oxygen signal as measured by a residual gas analyzer.

The oven nozzle consists of a hexagonal array of twenty-eight capillaries (1.14-mm diameter, 48.3 mm length) packed into a triangular aperture.\(^22\) In order to meet the density requirements 1 cm downstream from the oven to ignite a self-sustained discharge, the oven was operated at a temperature of 650°C, yielding a beam with a calculated total flux.

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of $2 \times 10^{17}$ atoms/s and mean speed of 823.5m/s, assuming a Maxwell-Boltzman velocity distribution$^{20,23-25}$ Under these conditions, the effects of interatomic collisions on the beam dynamics may not be neglected and it is anticipated that the centerline intensity will be attenuated in proportion to the square root of the Knudsen number in conjunction with a broadening of the angular distribution of the beam.$^{25}$ The resultant angular spread of the beam was quantified using a quartz crystal thickness monitor from INFICON with a 1mm aperture at the position of the surface ionization apparatus, approximately 26cm downstream from the oven opening. The deposition data collected as the thickness monitor was scanned across the beam is shown in Fig. 2. The best fit to the data resembles the anticipated angular distribution of an effusive beam emanating from a single channel with an aspect ratio approximately 3.5 times less than the capillaries used in our source. This broader distribution is the result of using multiple capillaries at the oven opening and operating the oven in what is referred to as the transitional, or opaque, flow regime.$^{25}$ The enhanced number of atomic collisions resulting from both of these factors manifested as a broadening of the angular distribution of the beam. From this distribution, about 0.29% of the atoms in the beam impinge on the surface of the hot wire in the surface ionization apparatus per second.

### III. RESULTS AND DISCUSSION

In lieu of a laser to pump the $4s^2 \text{^{1}S_0} \rightarrow 4s4p \text{^{3}P_1}$ inter-combination transition in calcium, we implemented a hollow-cathode discharge to populate the metastable $\text{^{3}P_1}$ triplet. The discharge scheme consisted of a toroidal tungsten cathode and two high voltage anodes. The anodes are positioned approximately at approximately 2cm increments from the grounded oven opening. 80% transmission wire meshes were spot welded across the opening of the anodes. Igniting a glow discharge depends largely on the electrode spacing and, more importantly, on the density of the gas between the electrodes. The experimental conditions must guarantee that the electron free path through the gas between the electrodes is long enough to enable the electrons to acquire the necessary kinetic energy for ionizing an atom and short enough to support multiple collisions before the electrons impinge on the anode. Since the gas density can be more easily modulated in-situ via the temperature, Giusfredi et. al. provide a lower limit for producing a self-sustained glow discharge$^{20}$

$$n \geq \frac{1}{l\sigma_i} \sqrt{\frac{m_e}{m_i}},$$

where $n$ is the atomic density, $l$ is the distance between the electrodes, $\sigma_i$ is the electron-impact ionization cross section, $m_e$ is the electron mass, and $m_i$ is the ionic mass. These experimental conditions support an avalanche chain reaction of ionization events – a necessary prerequisite of a glow discharge. The transition to a self-sustaining glow discharge is accomplished when (a) the energy loss due to inelastic collisions with the gas atoms is recouped from higher external electric fields and (b) electron losses at the anode are compensated by enhanced electron emission at the cathode. The cathode may emit additional electrons due secondary electron emission resulting from the impact of high energy ions or thermionic emission (i.e., a hot cathode)$^{26-28}$ At our discharge length of $l \approx 2$ cm, and an ionization cross section of $\sigma_i \approx 5 \text{Å}^2$, the minimum atomic density for calcium is $\sim 3.7 \times 10^{18}$ atoms/m$^3$. Naturally, due to the free expansion of the vapor into the vacuum chamber, the beam density outside of the oven will be

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**FIG. 1.** Diagram of the experimental setup (not to scale). O: capillary oven heated by a heater cable wrapped around its body to about 650°C. C: discharge cathode consisting of a 0.25mm-diameter toroidal tungsten wire operated at 8.46W. A: discharge anodes with a wire mesh spot-welded across their openings. I: ion extraction plates. S: surface ionization apparatus consisting of a stainless steel tube (ion detector) with a lateral rectangular cut and a coaxial hot tungsten wire (ionizing surface). M: mirror (other imaging optics not shown). F: bandpass filter centered around 442nm. P: photomultiplier tube.

**FIG. 2.** Angular distribution of the atomic beam at the position of the SIA. Deposition rate data was collected at various positions with a thickness monitor while the discharge was on. The error bars denote the standard error in the deposition rate over a time span of five minutes. The red-dashed distribution is a best-fit to the data and corresponds to the distribution of an effusive source emanating from a channel with an aspect ratio 3.5 times less than the capillaries used in this experiment.$^{25}$
significantly lower than \( n = p(T_{oven})/kT_{oven} \). The density profile of an atomic beam drops by up to two orders of magnitude in the discharge region. For example, Fig. 3 demonstrates the calculated longitudinal density profile of a single capillary. Consequently, the oven temperature must be sufficiently high to guarantee that the beam density meets the condition above for a glow discharge. We found this temperature empirically to be about 650°C.

The electron-atom collisions within the discharge can impact several beam properties, particularly the beam angular spread and velocity distributions. Collisions between atoms and electrons traveling in the forward direction parallel to the atomic beam will simply result in a small longitudinal momentum transfer to the atom. In the event that an electron is scattered through some finite angle, the atom will receive a transverse momentum kick, which will manifest as a net increase in the angular spread of the beam, albeit by a small amount. Rundel, et. al. reported that electron-atom collisions in their discharge resulted in a 1.4° increase in the full-width half-maximum in the angular distribution of their metastable noble gas beam. Furthermore, we expect a shift toward higher velocities in the velocity distribution of the beam as slower atoms will sustain greater angular deflections than faster atoms and consequently be more strongly attenuated.

In order to investigate the surface ionization of metastable atoms, it was necessary to quantify the fraction of atoms in the beam excited to metastable states. Considering the diffuse fluorescence signal of the decay of the \(^3P_J\) state and the excessive background noise at this wavelength from the blackbody radiation of the oven, it proved impractical to use the fluorescence of the intercombination transition to estimate the total number of metastable atoms in the beam. We instead used a photomultiplier tube (Hamamatsu R212) and a bandpass filter (Edmund Optics part no.: 65-684) centered around 442nm to measure the intensity of the \(^3D_J \rightarrow ^3P_J\) transitions as the background noise at these wavelengths was greatly reduced. The solid angle of our optical system was limited by a lens succeeding the mirror in Fig. 1 (not shown) to 0.04 sr, limiting the optical throughput of the system to approximately 0.23%. The dependence of this signal on the potential of the discharge anode with a constant current on the cathode is shown in Fig. 5. The presence of the cathode as a source of thermionic electrons was found to not have a significant impact on the \(^3D_J \rightarrow ^3P_J\) transition intensity, as the glow discharge was readily ignited with the high voltage anodes alone. Of the \(2 \times 10^{17}\) atoms/s produced by the oven under aforementioned conditions, it is estimated that approximately 0.24% of the atoms undergo these transitions to the metastable \(^3P_J\) triplet. This is strictly a lower limit to the number of metastable atoms in the beam following the discharge for two reasons: not all atoms decay to the metastable triplet via \(^3D_J\) states and our detection system is insensitive to the metastable \(^1D_2\) singlet state, which is also expected to undergo surface ionization along with the atoms in the \(^3P_J\) states. Furthermore, any ions produced by the discharge are extracted from the beam by a pair of parallel plates to prevent them from masking the surface ion signal at the SIA.

The design of the SIA has been described in more detail in an earlier article and is depicted in Fig. 6. The SIA consists

![Figure 3](https://example.com/fig3.png)

**FIG. 3.** Longitudinal density profile of a beam emanating from a single capillary with diameter \(2r = 1.14\) mm and length \(L = 48.3\) mm. The density along the axis of the capillary, \(n(z)\), has been scaled by the density of the vapor within the reservoir, \(n_0\). The entrance and exit of the capillary have been marked by dashed lines at \(z = 0\) and \(z = L\), respectively.

![Figure 4](https://example.com/fig4.png)

**FIG. 4.** Energy level diagram for calcium. The states we aim to populate with the discharge are the \(^3P_J\) states.

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>Wavelength (nm)</th>
<th>(A) (s(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1S_0)</td>
<td>(^1P_1)</td>
<td>422.8</td>
<td>2.18 \times 10^8</td>
<td>32</td>
</tr>
<tr>
<td>(^1P_1)</td>
<td>(^1D_2)</td>
<td>5547</td>
<td>2180</td>
<td>32</td>
</tr>
<tr>
<td>(^1D_2)</td>
<td>(^1S_0)</td>
<td>457</td>
<td>40</td>
<td>32</td>
</tr>
<tr>
<td>(^3D_2)</td>
<td>(^3P_{1/2})</td>
<td>657.4</td>
<td>96-300</td>
<td>32</td>
</tr>
<tr>
<td>(^3P_{1/2})</td>
<td>(^1S_0)</td>
<td>657.4</td>
<td>2300</td>
<td>33, 34</td>
</tr>
<tr>
<td>(^3D_{1/2})</td>
<td>(^3P_{1/2})</td>
<td>442.7-445.8</td>
<td>10^7</td>
<td>35</td>
</tr>
</tbody>
</table>

**TABLE I.** Wavelengths and rates of spontaneous decay for relevant transitions in calcium.
of a hot, ionizing tungsten wire surrounded by a cylindrical stainless steel ion detector (collector) with a lateral rectangular cut to allow the atomic beam to be deposited onto the wire. Prior to any measurements, the hot wire was preconditioned for several hours at an approximate temperature of 2000 K. We measured the work function of the tungsten hot wire by measuring the thermionic emission of electrons at various temperatures. Throughout these measurements, the SIA was not exposed to the calcium beam. A Richardson plot of the data is displayed in Fig. 7, where the slope of the best fit to the data in the Richardson regime (in contrast to the space-charge or field-limited regime) yields the work function $\Phi = 5.18 \pm 0.03$ eV. This elevated value compared to the accepted work function of clean polycrystalline tungsten (4.54 eV) is likely a result of partial surface oxidation. Indeed, at a background pressure of $10^{-7}$ Torr, we may expect an increase in the tungsten work function of up to $\sim 0.9$ eV.\(^{37}\)

Nonetheless, this work function change should not constitute a significant problem. According to Eq. 1 and elemental surface ionization theory, even with partial oxidation, it is still expected that the metastable calcium atoms be surface ionized with a much greater efficiency than the ground state atoms. Here, it should also be noted that the work function measurements via the positive thermal ionization of gaseous atomic species with known ionization energies are in general agreement with those of thermionic emission of electrons.\(^{1,8,10,38-40}\)

In addition to its effect on the work function, oxidation will have an additional impact on surface ionization efficiency through its effect on desorption dynamics and chemical reactivity at the surface. For ground-state calcium atoms on a rhenium hot wire, Stienkemeier, et. al., report a diminished surface ionization efficiency at wire temperatures exceeding $\sim 1900$ K, which they attribute to enhanced oxide formation.\(^5\) Since we can only assume that metastable calcium atoms and their ensuing ions will also exhibit increased reactivity with oxygen at these temperatures, we operated our tungsten hot wire at a temperature of 1750 K.

Furthermore, surface contamination is known to affect desorption lifetimes.\(^{31}\) The mean residence time $\tau_{i,a}$ of an atom or ion adsorbed on a surface with adsorption energy $E_{i,a}$ at temperature $T$ is given by the Arrhenius equation:

$$\tau_{i,a} = \frac{\tau_0 e^{E_{i,a}/k_B T}}{T},$$

where $\tau_0$ is a desorption time constant on the order of $\sim 10^{-16} - 10^{-13}$ s depending on the surface mobility of the adsorbates.\(^5,6,42\) Calcium and other alkaline earth atoms exhibit relatively more localized behavior with a prefactor $\tau_0$ on the order of $10^{-13}$ s. For alkali atoms, it has been demonstrated that the desorption time decreases with an increase in the oxidation of the surface since the oxygen serves as an intermediate layer, effectively increasing the distance between the alkali atoms and the hot wire surface.\(^{31}\) Presumably, this effect is present between the calcium atoms and our partly oxygenated tungsten wire. Ultimately, the desorption time of the metastable calcium atoms must be sufficiently long to allow for surface ionization, while not exceeding some limit beyond which the ion may be neutralized through an additional charge exchange interaction before evaporating from the hot wire. Further work needs to be done in order to establish the optimal desorption conditions for the surface ionization of metastable atoms.

The work function measurements of Fig. 7 were performed under a background pressure of $10^{-7}$ Torr and while the calcium beam was obstructed. The reasoning for the latter is that the electric field between the electrodes in the SIA (that is, the tungsten hot wire and the surrounding detector) was reversed during the work function measurements to enable to emission

![Figure 5](https://example.com/fig5.png)

FIG. 5. Fluorescence signal from the 442 – 446 nm decays of the $3^2 D_J \rightarrow 3^2 P_J$ transitions. At saturation, approximately 0.24% of the atoms undergo these transitions.

![Figure 6](https://example.com/fig6.png)

FIG. 6. (a) Bare tungsten hot wire and (b) the fully assembled SIA. The tungsten hot wire is spot welded onto two molybdenum pieces, one of which is extendable to accommodate any change in strain resulting from the thermal expansion of the hot wire. The hot wire is surrounded by a cylindrical stainless steel ion detector (collector) with a lateral rectangular opening to allow the atomic beam to impinge on the hot wire. Custom-machined ceramic parts were used to isolate the hot wire and collector from the grounded frame on the exterior of the SIA.
of thermionic electrons. Specifically, the hot wire was floated to 100 V and the surrounding detector was grounded. The calcium beam was obstructed because this electric field would hinder the evaporation of any ions formed at the surface, leading to an anomalous accumulation of calcium ions on the hot wire that is not otherwise present in this experiment. Naturally, the accumulation of neutral calcium may still occur during the work function measurements as well as the rest of the experiment since it is independent of the electric field within the SIA. However, since the hot wire temperature is much greater than that of the calcium oven, neutral calcium accumulation on the tungsten surface is insignificant since the rate of evaporation exceeds the rate of adsorption. In any case, we want to emphasize that the results in Fig. 7 were consistent with time and reproducible under the experimental conditions mentioned above.

Fig. 8 presents the dependence of the surface ionization signal at the SIA on the potential of the discharge anode. When collecting this data, the discharge cathode was heated to the same temperature as in Fig. 5 and the field between ion extraction parallel plates was maintained at 200 V/mm. In contrast to the aforementioned work function measurements, the surface ion current was anticipated to be several orders of magnitude less than the thermionic electron current. We correspondingly used a Femto low noise transimpedance amplifier with a variable gain, which allowed the stainless steel detector to be floated at $-10$ V. The detected surface ion current increased with the voltage on the discharge anode until saturating at about 400 V, the same saturation voltage in Fig. 5.

To demonstrate that the SIA ion signal in Fig. 9 is due exclusively to the surface ionization of metastable atoms and is not obscured by ions originating from the plasma in the discharge, we operated the discharge with 1kV on the discharge anode and modulated the field between the ion extraction plates. From the discharge fluorescence measurements in Fig. 5, we estimated that about 0.24% of the atoms in the beam were excited to the $^3P_J$ states at these conditions and that some fraction of the atoms were ionized by electron bombardment. With no field between the ion extraction plates, the SIA ion signal was overwhelmed by the discharge ions. As the ion extraction field increased, the SIA ion signal quickly decreased to approximately 500nA. Naturally, modulating the ion extraction field while the discharge was off did not have a noticeable effect on the SIA signal. Ion extraction fields of 25 V/mm and above are sufficiently strong to deflect all discharge ions and preclude them from impinging on the SIA ion collector. The 500nA current is readily attributable to the surface ionization of metastable calcium atoms.

At the aforementioned operating conditions (oven temperature 650 °C, discharge anode voltage 1kV, constant discharge cathode temperature), fluorescence measurements indicated that approximately 0.24% of the atoms in the atomic beam are excited to a metastable state. From the data in Fig. 2, approximately 0.29% of the total flux of emitted atoms impinge on the 0.25 mm-diameter hot wire positioned at a distance of 26 cm from the oven opening. It follows that $1.4 \times 10^{12}$ metastable atoms land on the tungsten hot wire per second. Recall this is a lower limit to the number of metastable atoms in the beam as not all atoms decay to the metastable triplet via the the $^3D_J \rightarrow ^3P_J$ transitions and our detection system is insensitive to the metastable $^1D_2$ singlet state, which is also expected to undergo surface ionization along with the atoms in the $^3P_J$ states. The work function of the polycrystalline tungsten hot wire was determined through thermionic emission to be $\Phi = 5.18 \pm 0.03$ eV – an appropriate value that exceeds the ionization energy of the metastable state, while maintaining a sufficiently low probability of ionization for the ground state atoms. Indeed, according to Eq. 1, we may expect up to 0.5% of ground state calcium atoms impinging on the tungsten hot wire to undergo ionization. This current manifests as a con-

![Fig. 7. A Richardson plot of thermionic emission of electrons from a polycrystalline tungsten hot wire. For the work function measurement, the hot wire was floated to 100 V and the surrounding stainless steel detector was grounded through an ammeter. The slope of the thermionic electron current with respect to temperature in the Richardson regime yields the work function of the wire. The data for temperatures above 1700 K are evidently space-charge limited.](image1)

![Fig. 8. Surface ion signal at the SIA as a function of the discharge anode voltage. The field between the ion extraction plates was 200 V/mm. As the discharge anode voltage increased, the fraction of metastable atoms in the beam inferred from the fluorescence data in Fig. 5 also increased, until reaching saturation at 400 V.](image2)
Despite these limitations in the fluorescence measurements, the experiment outlined in this report indicates that metastable calcium atoms experience a high degree of ionization on a tungsten surface and we may conclude that the efficiency of the surface ionization of metastable calcium atoms is appreciably higher than that of the corresponding ground state atoms. Effectively, metastable atoms can be selectively ionized by a hot metal surface with an appropriate work function. This has potential applications for improved signal-to-noise ratios in frequency standards by using a single laser to pump clock transitions in alkaline earth and alkaline earth-like systems, followed by selective surface ionization to detect the excited atoms.

Here, it is necessary to acknowledge potential limitations to the applicability of this selective surface ionization mechanism to other atomic species. This report demonstrates that to a large extent, it is the relationship between the effective ionization energy of the metastable state and the surface work function that determines the probability of surface ionization. However, in the event that the excitation energy of the metastable atom is comparable to or exceeds the work function of the surface, additional charge exchange processes may occur, specifically Auger neutralization. Auger neutralization will occur with a high probability if the ion recombination energy to the ground state exceeds double the work function, $E^+ \geq 2\Phi$, at which point an electron from the metal surface tunnels to the vacant ground state of the surface ion. The excess energy from Auger neutralization simultaneously excites a separate electron to a higher energy band in the metal. If the excess energy is sufficiently high, this Auger electron may be ejected from the metal and used in spectroscopy or for metastable atom detection.\cite{44,45,47} A process such as Auger neutralization preclude the use of surface ionization in the applications mentioned above for certain atomic species (e.g., metastable noble gas atoms, which are readily neutralized following ionization). While surface ionization may too be used for metastable atom detection (through ion emission, in contrast to electron emission),\cite{48} ion emission is necessary for application to atomic clocks and isotope enrichment, which necessarily require the surface ion to desorb from the surface without undergoing a neutralizing charge exchange. In the case of the isotope enrichment of calcium, for example, atoms of a particular isotope such as Ca-48 may be optically pumped to the metastable $^3P_J$ state. These metastable atoms may then be selectively ionized at a hot surface with a high work function and subsequently guided to a collector. Such a scheme would not be feasible for certain atomic species with a high probability of undergoing Auger neutralization after ionization, such as metastable noble gas atoms.\cite{44,47}

IV. CONCLUSION

In conclusion, we have demonstrated that metastable calcium atoms undergo surface ionization on a hot tungsten surface with a markedly greater efficiency than ground state calcium atoms. Here, we excite a fraction of calcium atoms in a thermal beam to metastable $^3P_J$ states through a glow discharge and we estimate the number of metastable atoms by detecting the fluorescence of the decays of higher-lying $^3D_J$ states. These measurements provide an underestimate for the

![Graph](image_url)

**FIG. 9.** Surface ion signal as a function of the field between the ion extraction plates. For the black data set, the discharge anode was held at a potential of 1000 V. At an ion extraction field of zero, ions produced by electron bombardment in the discharge are detected by the SIA and mask the metastable atom surface ion signal. Increasing the potential difference between the ion extraction plates progressively deflected the discharge ions away from the SIA, revealing a finite signal corresponding to the surface ionization of metastable calcium. The white data set was collected under the same conditions, albeit with a discharge anode voltage of 0 V.
fraction of metastable atoms in the beam. The ground and excited atoms then impinge on a polycrystalline tungsten hot wire with a work function measured to be $\Phi = 5.18 \pm 0.03$ eV. Ions evaporating from the hot wire surface are then detected as a current by a stainless steel sheath enveloping the hot wire. In light of the fact that the fluorescence measurements inherently underestimate the flux of metastable atoms in the beam, it is evident that the surface ionization of metastable calcium atoms is high. These results can be used to develop novel isotope enrichment methods and compact atomic clocks. In particular, stable isotopes of calcium have garnered appreciable attention for their use in medicine and basic scientific research.16–19 These applications have, in turn, spurred several experiments focused on calcium isotopes.49–51

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.


Scaled density $\frac{n(z)}{n_0}$

Longitudinal position $z$ (mm)
\[ \begin{array}{ccc}
^1S_0 & ^1P_1 & ^1D_2 \\
\hline
^3S_J & ^3P_J & ^3D_J
\end{array} \]
(a) Extendable tag

Ceramic insulation

Tungsten hot wire

(b) Collector

Extendable tag
\[ T \approx 1700 \text{ K} \]
Surface ionization signal (A) vs. Ion repulsion plate E-field (V/mm)

- Solid line: Discharge on
- Dotted line: Discharge off

Surface ionization signal: $\times 10^{-6}$