

Rydberg States of Silver: Excitation Dynamics of Doped Helium Droplets

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Silver atoms, initially embedded in nanodroplets of superfluid helium (roughly 10^4 atoms in size), are found to move to the surface and desorb when excited to the broadened $5p$ level. The absorption of a second photon within less than 10 ns leads to the population of previously unobserved Rydberg states ($20 < n < 60$) of free silver atoms. This is the first result showing laser induced movement of a foreign atom from the inside to the surface of a nanodroplet of superfluid helium.

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Most of the fundamental properties of helium nanodroplets have now been experimentally verified and satisfactorily explained by theory. The temperature of a droplet formed in a free expansion in vacuum has been determined experimentally from the rovibrational spectrum of embedded SF_6 to be 0.37 K [1]. Recent results on the infrared absorption spectrum of doped helium clusters clearly demonstrate that droplets with as few as 60 ^4He atoms are superfluid [2]. With our present knowledge, the way is paved for the application of this cold, clean, superfluid environment to low temperature chemistry, condensed matter physics, high resolution spectroscopy, and the fundamental physics of finite, condensed Bose systems.

In a previous Letter, we published data on the single-photon absorption spectroscopy of silver atoms embedded in helium droplets [3]. In this Letter we report on an extension of that work, and present the first application of superfluid helium nanodroplets to the study of atomic Rydberg states. These results are not only the first measurements of previously unobserved Rydberg states of silver, but the dynamics we infer also have important consequences to the application of helium nanodroplets in other fields.

Depending on the specific form of the interaction potential between an individual helium atom and an impurity, the impurity may be either solvated inside the droplet or loosely attached to its surface. Whereas most molecules are drawn inside the liquid [4], alkali atoms reside on the surface [5,6]. In contrast, we have recently shown that silver atoms, despite their single valence s electron, are attracted sufficiently to the helium so that they are located inside the droplets [3]. The strongly broadened and blueshifted lines observed in our earlier experiments, and those observed in bulk helium, are usually explained by a bubble model, originally developed for free electrons in helium. Because of the Pauli repulsion between the closed-shell helium electrons and the impurity, a cavity is formed around the metal atom [7]. The expected size-dependent energy of the bubble provides a qualitative understanding of broadenings, and shifts to spectral lines of embedded atoms [8].

In our experiment, helium droplets following a log-normal size distribution with an average size of 10^4 atoms

are produced in a supersonic expansion of cold helium gas ($T = 12$ K) through a $5\ \mu\text{m}$ nozzle into vacuum. After skimming, the droplet beam passes through an oven containing a low pressure vapor of silver atoms. The temperature of the oven, and hence the vapor pressure, is adjusted to maximize the pickup of single silver atoms by the droplets. Following doping, the beam is collimated to 2 mm in diameter by a series of holes spaced at roughly 30 cm intervals along the machine. The doped droplets are spectroscopically investigated with pulses from a tunable laser propagating perpendicularly to the beam and then ionized, mass selected, and detected.

In our earlier work, the droplets were ionized by electron impact with 70 eV electrons after being probed by the laser pulse. The absorption of a photon by an embedded silver atom appeared as a depletion in the silver ion signal. A more detailed description of the experiment can be found in our previous Letter [3]. The present experimental setup is the same, except for the method of detection; we now use multiphoton absorption followed by field ionization to ionize the embedded impurity before mass selection by a high resolution time-of-flight mass spectrometer. The signals we record, and the physics we see, are quite different from our earlier work

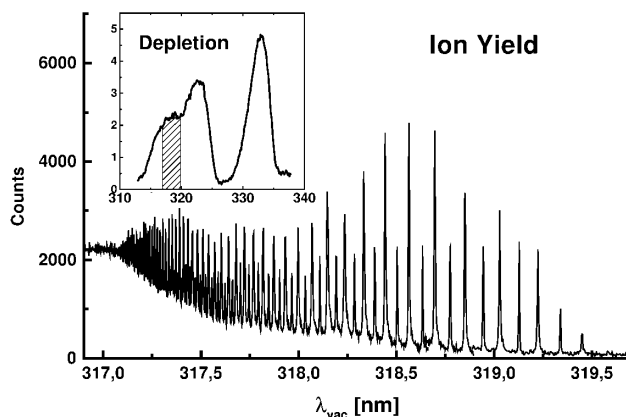


FIG. 1. Multiphoton ionization of doped helium droplets. The signal is dominated by silver ions. The inset shows the depletion signal obtained under comparable conditions [3].

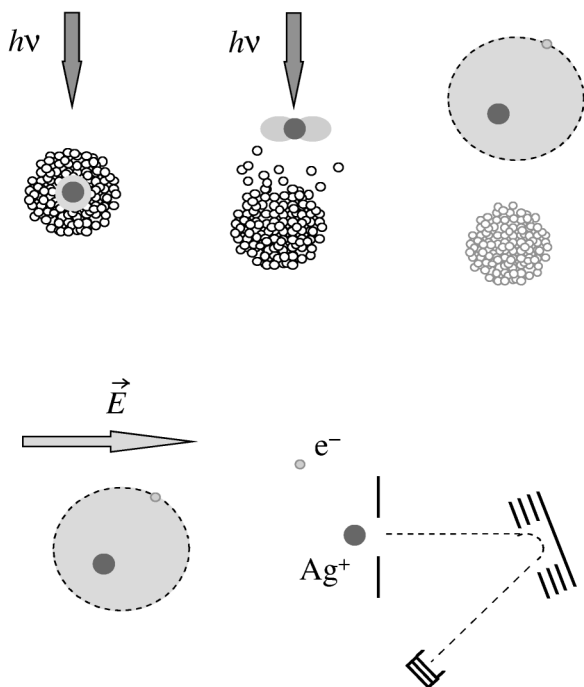


FIG. 2. Schematic of the excitation process: Silver atoms inside the droplets are excited to a broadened state, corresponding to the $5p$ level in the free atom. Because of a substantial change in the interatomic potential the excited atoms desorb from the droplets and may be further promoted by a second photon to a Rydberg level.

and provide the first observation of laser induced relocation of a foreign atom from the inside to the surface of a superfluid helium nanodroplet.

In Fig. 1, we show the yield of silver ions obtained with excitation of the doped helium droplets with 0.1 mJ laser pulses of 10 ns duration and 0.08 cm^{-1} bandwidth from a frequency doubled dye laser (Nd:YAG pumped LDL 20505). The pulses are weakly focused to a spot 1 mm in radius, defining an interaction volume of 4 mm^3 . The silver monomer is the dominant ion under these conditions. We observe a series of very sharp converging lines that has all the characteristics of a Rydberg series, in contrast to our previous depletion (single-photon absorption) results which show broad bands and no discernible fine-structure (inset of Fig. 1). We have checked for free atoms in our beam. There is no doubt that the signal is due to silver atoms embedded in helium droplets. There are no one- or two-photon transitions of the atom corresponding to the measured spectrum. The apparent ionization limit near 317 nm corresponds exactly to the energy required to remove an electron from a free *excited* silver atom.

We propose the following mechanism summarized in Figs. 2 and 3. Silver atoms inside helium droplets are excited into broadened $5p$ states. This absorption profile (inset of Fig. 1) is known from our depletion measurements to vary only slowly with frequency, and

we can safely assume a resonant process over the entire wavelength range discussed here. With a lifetime of about 7 ns [9], the free $5p$ state lives long enough to lead to a substantial rearrangement of the helium droplet [10]. As a consequence, the excited atom is forced out of the droplet on a time scale of several nanoseconds and relaxes to its unperturbed (excited) atomic state. The excited atoms may then absorb a second photon from the same laser pulse and populate the Rydberg resonances we observe in the ion yield. Ionization of these atoms is due to field ionization in our time-of-flight spectrometer. A comparison of our earlier single-photon data with the two-photon process presented here indicates that this is an efficient process for droplets on the order of 10^4 atoms in size; as far as we can tell, all atoms that absorb a photon move to the surface of the droplet. For the case of silver, this must be an important mechanism leading to the depletion signal in the one-photon experiment and probably dominates the evaporation mechanism proposed in our earlier work.

For high principal quantum numbers, external electrical fields can be comparable to the Coulomb field of the atom. The ionizing field is given by

$$E = \frac{1}{16n^4},$$

where E is taken in atomic units (27.2 V/a_0). The above formula ignores Stark shifts, which greatly complicate the picture [11]. Substituting an extraction voltage of 2000 V/cm indicates that we should be able to observe states with $n > \approx 20$. We assign the first line visible in Fig. 1 to the $n = 23$ Rydberg state, explaining the absence of transitions at wavelengths longer than 320 nm. Reducing the extraction potential in the first stage of the mass spectrometer suppresses the red part of the spectrum, confirming field ionization as the mechanism responsible for the production of ions from the Rydberg atoms. It should be noted, however, that in our experiment the absorption takes place in a field-free region; the extraction is switched on only after a delay.

In the spectrum, we can distinguish two series which are due to transitions of the excited $5p$ valence electron into ns and nd states. Both converge to the same ionization limit and appear as lines with alternating intensity in Fig. 1. A fit of a Rydberg formula, with quantum defect, yields the parameters listed in Table I. The ionization limit is calculated with a value of 29552.1 cm^{-1} for the excited $5p_{1/2}$ level [12]. Although we have observed some transitions originating from the $5p_{3/2}$, these are very much weaker than those originating from the $5p_{1/2}$. It is not evident why the $5p_{1/2}$ level should be the one preferentially populated after desorption from the droplet and not the $5p_{3/2}$ originally excited. A similar effect has also been observed in the fluorescence of silver atoms in bulk liquid helium. There the emission originates exclusively from the lower $5p_{1/2}$ state, presumably due

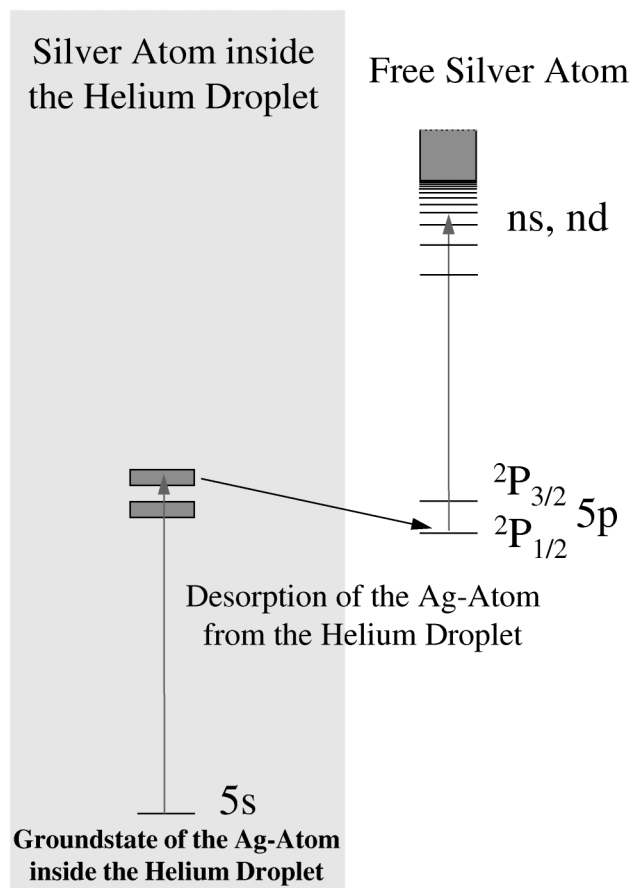


FIG. 3. Schematic level diagram of silver atoms in liquid helium. In the desorption process the atom relaxes to the free states shown on the right.

to fast nonradiative relaxation from the $5p_{3/2}$ mediated by the helium environment [13].

To our knowledge, none of the states shown here have been observed before. A detailed study of the absorption spectrum of silver has been performed by Brown and Ginter [14]. Their compilation lists Rydberg states with p symmetry up to $n = 70$. Single-photon transitions from the ground state to excited s and d states are electric dipole forbidden. Furthermore, two-photon processes in the free atom, aside from coincidences, are nonresonant, and Brown and Ginter observed only lower lying transitions of the d series ($n < 13$), and these at low intensities. The great advantage of our technique for these measurements is that all transitions are resonant two-photon transitions. The first is broad, ensuring a resonant process over the entire wavelength range. The second is sharp, giving high resolution spectra. The mechanism relies on the movement of the silver atom from the inside to the surface of the droplet after absorbing the first photon and before absorbing the second. From their data, Brown and Ginter extrapolate an ionization potential of 61106.6 cm^{-1} . For the d series they determine a typical quantum defect of 2.0 ($n = 10$). A recent laser study of silver reports a value of

TABLE I. Parameters of the $5p \rightarrow ns, nd$ Rydberg series, assuming a value of 29552.1 cm^{-1} for the $5p$ level.

Series	Ionization limit	Quantum defect	Linewidth
s	$61106.(8) \text{ cm}^{-1}$	3.6(0)	0.5 cm^{-1}
d	$61106.(8) \text{ cm}^{-1}$	2.1(4)	1.0 cm^{-1}

61104.3 cm^{-1} for the ionization potential [15]. Because of the multistep excitation scheme chosen in that experiment, only p ($n < 60$) and f states ($n < 33$) were observed. These authors note a discrepancy of 2 cm^{-1} to older tabulated ionization data but give no explanation. Our data was calibrated against a neon/iron hollow cathode lamp, resulting in a systematic error of less than 1 cm^{-1} . This is in perfect agreement with the values reported by Brown and Ginter. Quantum defects for lower members of the s and d series ($n = 5-10$) were reported in a study of lifetimes of neutral silver [16]. The authors found values of 3.5 and 2.0, respectively.

The location of foreign atoms inside or on the droplet surface is the key to the physics and chemistry that can be studied using the cold, superfluid environment provided by a helium nanodroplet in vacuum. We have previously reported the use of helium droplets for the preparation of large, mass selected, ultracold metal clusters which we plan to exploit in high resolution spectroscopic studies of their electronic and superconducting properties. The production of large metal clusters relies on the metal atoms being located inside the droplets [3]. In contrast, the Scoles group at Princeton have used helium droplets for the preparation and spectroscopic study of high spin states of small, free sodium clusters [6]. Their technique relies on the sodium atoms being located on the surface of the droplet. There have been suggestions to exploit the large thermal conductivity, characteristic of the interior of superfluid helium droplets, to study energy transfer in chemical reactions under single collision conditions [17]. By exciting the silver atom, we adjust the silver-helium potential surface, and the silver atom moves from the inside of the droplet to the outside. This is the first result showing the laser induced movement of a foreign atom in or on a droplet. The movement is over a length scale of 10 \AA . We expect in the future to be able to influence the progress of chemical reactions using this technique. A simple example is the control of the rate of metal cluster growth inside helium droplets by bathing the pickup region with resonant UV light. High intensity light at about 318 nm should strongly inhibit or halt the growth of a silver cluster. Although it is clear that this will work for silver, further experiments are necessary to establish the general applicability of the technique.

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