

## Unusual Rydberg System Consisting of a Positively Charged Helium Nanodroplet with an Orbiting Electron

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Evidence is presented of an unusual Rydberg system consisting of a helium nanodroplet containing a positively charged sodium ion and an orbiting electron. Rydberg states of this system with principal quantum number  $n < 20$  are found to be unstable on a nanosecond time scale. In contrast, Rydberg states with  $n \geq 100$  are found to have a lifetime of  $1.1 \mu\text{s}$ . In addition, it is found that the ionization threshold of sodium-doped helium is broadened and redshifted with respect to that of the free atom. These observations are successfully reproduced using a pseudodiatomic description of the system in which the interactions of the sodium and its ion with the helium are calculated as the sum of pair potentials.

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The extraordinary properties of Rydberg states have attracted attention from various fields of science, ranging from particle physics [1] to quantum information processing [2]. For example, within the realm of quantum information processing, Rydberg atoms have been proposed for coupling atomic to mesoscopic systems [3]. The long radiative lifetime of Rydberg states is not only essential for this specific example but also for many other applications. Questions regarding the stability of Rydberg systems interacting with objects be it microscopic or macroscopic are thus pertinent. Here we consider a system comprising a sodium atom located on the surface of a helium nanodroplet consisting of typically  $\sim 10^4$  atoms which is excited to Rydberg states with principal quantum numbers  $n \geq 7$ .

Previous studies of alkali-doped helium nanodroplets have mainly focused on the  $np$ - $ns$  transitions [4,5], only recently studies involving higher excited states were reported [6,7]. For all these systems, with the exception of rubidium [8], excitation of the alkali atom yields an unstable system which leads to the desorption of the excited atom from the surface of the droplets [9,10]. Calculations indicate that this is the results of a strong repulsive interaction of the localized Rydberg electron with the helium [11]. The interesting question that poses itself, and that we will address here, is if a stable system can result when the atom is excited to a Rydberg state with a large principal quantum number that interacts less strongly with the helium. This question has been addressed theoretically in relation to Rydberg states of pure helium droplets [12]. The authors conclude that due to a 1 eV potential barrier for electron penetration into liquid helium these states should be stable. However, recently Ancilloto *et al.* [13] discussed the stability of a similar system and argued that the electron orbiting outside the droplet may pull the positive ionic core close enough to the surface that fast electron-ion recombination occurs, thereby questioning the stability of such a system. Experimentally, Rydberg states

of pure helium droplets have been investigated using fluorescence spectroscopy [14]. In those studies Rydberg states with principal quantum number up to  $n \sim 8$  were observed but no details on their stability could be obtained. Rydberg states have also been invoked to explain certain aspects of the ionization dynamics of pure helium droplets [15]. To address the issues raised above, we here explicitly explore the properties of Rydberg states with high principal quantum numbers.

The experimental setup and spectroscopic techniques used are described in detail elsewhere [16,17]. In short, helium droplets are formed by expanding high-pressure helium gas into vacuum through a  $5 \mu\text{m}$  orifice cooled to cryogenic temperatures. The size distribution of the droplets can be systematically varied by changing the source temperature [18]. The helium droplets pick up Na atoms by traversing an oven in which metal sodium is evaporated. At the center of a velocity map imaging setup the Na-doped helium droplets are excited by the output of a dye laser system. Depending on the excitation wavelength and thereby the outcome of the photoexcitation, different detection schemes are applied. Absorption spectra of unstable Rydberg states are recorded using the same technique that has been used to record the absorption spectra of low excited states [6]. Photoelectron spectroscopy has been used to determine the ionization threshold and ZEKE spectroscopy is employed for the investigation of the ionization threshold and the characterization of Rydberg states with large principal quantum numbers [19]. In the present ZEKE experiments a pulsed electric field of 5 V/cm is applied typically  $1 \mu\text{s}$  after photoexcitation to ionize highly excited Rydberg states.

Excitation spectra of sodium-doped helium droplets ( $\text{Na-He}_N$ ) in the energy range just below the ionization threshold have been recorded by monitoring the yield of the most abundant photoproducts, i.e.  $\text{Na}^+$  and  $\text{Na}^+\text{He}_m$  ( $m = 1-4$ ). The spectra of the different photoproducts

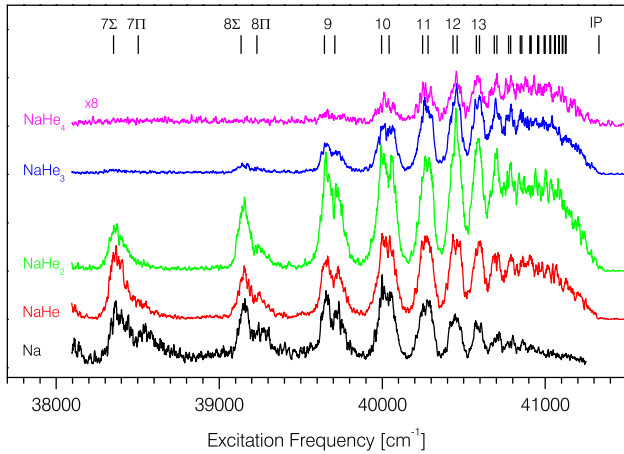


FIG. 1 (color online). Excitation spectra of sodium-doped helium droplets with a mean radius of 41 Å recorded by monitoring the yield of  $\text{Na}^+$  and  $\text{Na}^+\text{He}_m$ .

shown in Fig. 1 differ only by the relative intensities of the resonances and are all characterized by a regular series of peaks consisting of two components which merge into a single peak and eventually into a continuum. When assigning these spectra it should be realized that for the  $\text{Na-He}_N$  system not the valence electron's orbital angular momentum, but its projection onto the axis defined by the sodium atom and the center of the helium droplet,  $\Lambda$ , is a conserved quantity. Taking into account the  $\Delta\Lambda = 0, \pm 1$  selection rules for one-photon absorption, we assign the spectral lines to transitions from the  $3\Sigma$  ground state to  $n\Sigma$  and  $n\Pi$  Rydberg states, with  $n$  the principal quantum number of the  $\text{Na-He}_N$  system. The assignment of the resonances as indicated in Fig. 1 is based on the extrapolation of the analysis of spectra involving excited states with principal quantum numbers  $n \leq 6$  [6]. The individual resonances have been fitted to Gaussian profiles to determine their widths and positions. The widths are found to be largely independent of excitation frequency and amount to  $\sim 65 \text{ cm}^{-1}$ . The position of the resonances belonging to the  $\Sigma$  and  $\Pi$  series have been fitted to the analogue of the Rydberg formula:  $E_n = IT - R_\infty / (n-d)^2$ , where  $E_n$  is the energy of the level with the principal quantum number  $n$ ,  $IT$  the ionization threshold of the Na-doped helium droplet,  $R_\infty$  the Rydberg constant, and  $d$  the quantum defect. With the assignment of the resonances as discussed above we find an ionization threshold of  $41\,336 \pm 12 \text{ cm}^{-1}$  which is  $113 \text{ cm}^{-1}$  below that of free Na [20]. Spectra recorded at different droplet sizes reveal slightly different ionization thresholds, see Fig. 2. Analysis of the spectra furthermore yield a quantum defect  $d_\Sigma = 0.93 \pm 0.01$  for the  $\Sigma$  states and  $d_\Pi = 0.77 \pm 0.02$  for the  $\Pi$  states. The values of both these quantum defects are very close to that of  $np$  states of the free sodium atom,  $d_p = 0.85$  [21] indicating that the major contribution to both the  $n\Sigma$  and  $n\Pi$  states of the  $\text{Na-He}_N$  system originates from atomic  $np$  states [6,11]. The slightly larger value of the quantum defect for the  $\Sigma$  states indicates that atomic  $ns$  states,

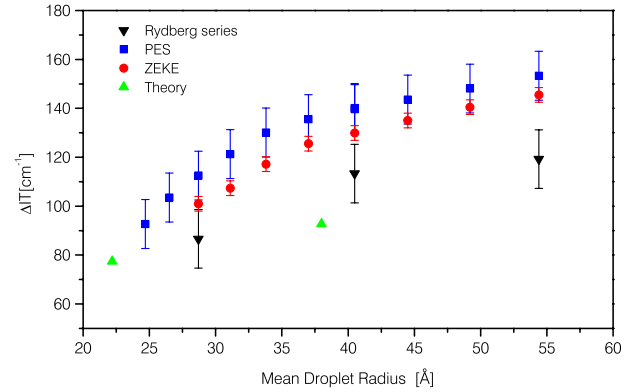


FIG. 2 (color online). Redshift of the ionization threshold of helium doped droplets with respect to the atomic threshold at  $41\,449 \text{ cm}^{-1}$  [20] as determined by different spectroscopic techniques and predicted by theory.

which have a quantum defect of  $d_s = 1.35$  [21], contribute significantly to these states. In contrast to the ionization threshold, the quantum defects do not depend on the size of the droplets.

Before characterizing the nature of high Rydberg states, we first investigate the direct photoionization of Na-doped helium droplets. In the upper panel of Fig. 3 we report the photoelectron spectrum of  $\text{Na-He}_N$ , and for comparison that of free Na. The  $\text{Na-He}_N$  photoelectron spectrum consists of a broad feature whose center is  $133 \text{ cm}^{-1}$  higher in energy than the narrow peak corresponding to the free Na atom, indicating that compared to the free atom the ionization threshold of  $\text{Na-He}_N$  is lowered by this amount. The shift of the ionization threshold reveals a systematic variation with droplet size; see Fig. 2. We use ZEKE spectroscopy to obtain more precise information on the ionization threshold. The middle panel of Fig. 3 shows the ZEKE spectra of sodium-doped helium droplets. The sharp feature at  $41\,445 \text{ cm}^{-1}$  can be assigned to the ionization threshold of free sodium atoms that are present as background gas [20]. The broad (FWHM  $\sim 65 \text{ cm}^{-1}$ ) peak centered at  $\sim 41\,320 \text{ cm}^{-1}$  corresponds to the ionization threshold of the Na-doped helium droplets. Comparison of the ionization thresholds as determined from excitation, photoelectron and ZEKE spectra, see Fig. 2, reveals that all three methods essentially yield the same values, indicating that they all three probe the same threshold. The lowering of the ionization threshold of a chromophore in helium droplets has been attributed to polarization effects and can be reproduced by the dielectric continuum model [22]. Here we use a more sophisticated method based on the pseudodiatomic model used to reproduce the excitation spectra of alkali-doped helium droplets [4]. In this model the interaction between the sodium atom and the helium droplet is reduced to a one-dimensional potential which is calculated as the sum of alkali-He pair potentials. Accordingly, we first calculate the effective potentials for the neutral and ionized system using available NaHe and  $\text{Na}^+\text{He}$  pair potentials [23,24] and the helium density

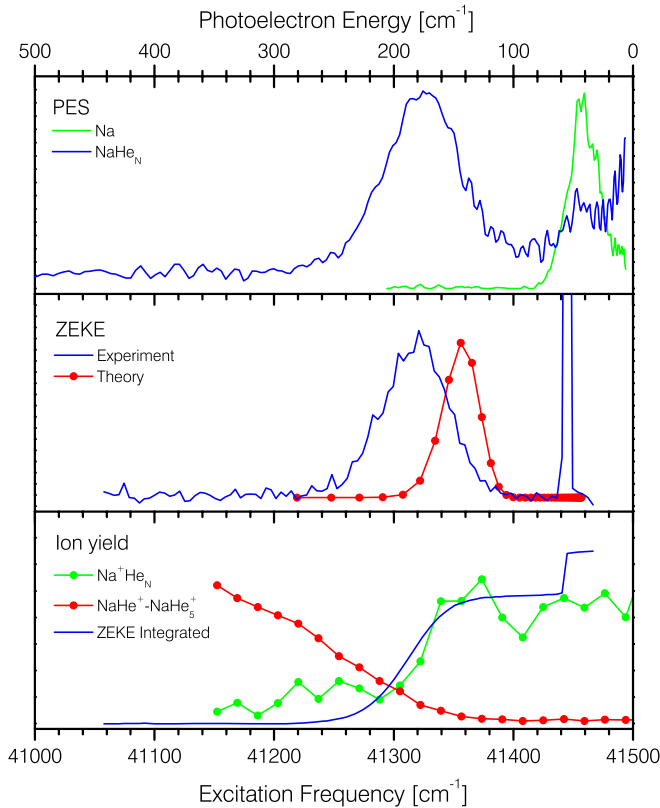


FIG. 3 (color online). Upper panel: Photoelectron spectra of sodium-doped helium droplets with a mean radius of 41 Å and free sodium atoms following two-photon ionization at  $20742\text{ cm}^{-1}$ . Middle panel: ZEKE spectrum of sodium-doped droplets and the calculated ionization spectrum for a droplet consisting of 5000 helium atoms. Lower panel: Integrated ZEKE spectrum and ion-yield spectra recorded by monitoring  $\text{Na}^+\text{He}_m$  ( $m = 1-5$ ) exciplexes and ion containing helium droplets.

profile for  $\text{Na-He}_N$  [5]. The excitation spectrum is then calculated as the envelope over the Franck-Condon factors between the lowest vibrational state of the neutral and vibrational states of the ionic system [25]. The agreement between the calculated and experimental spectra shown in Fig. 3 is rather good. The small discrepancies are probably related to accuracy of the pair potentials used. Based on the simulations, we conclude that the width of the ionization threshold as manifested in the linewidth of the resonances in the excitation and ZEKE spectra is largely determined by the delocalization of the sodium atom.

In the ZEKE experiments highly excited Rydberg states are created which are subsequently field ionized. The principal quantum numbers of these states can be estimated from the ionizing electric field to equal  $n \geq 100$  [26]. The classical electron orbit radii for these states are 3 orders of magnitude larger than the helium droplet radius. This implies that the  $\text{Na}^+$  ionic core is left essentially free on the surface of helium droplet with the electron orbiting the droplet. Before discussing the stability of this system in detail, we first address the fate of the  $\text{Na}^+$  core. The direct way to determine whether the ionic core remains attached

to the droplet would be to use the mass-selected variant of ZEKE [27]. However, the large mass of helium droplets prohibits a successful implementation of this technique. Instead we make use of the fact that the ZEKE spectrum of a given species is the energy derivative of the ion-yield spectrum of that species. For this purpose we have recorded ion-yield spectra for two different mass ranges. The first range covers 27–43 amu and corresponds to  $\text{Na}^+\text{He}_m$  exciplexes with  $m = 1-5$ . The second range covers 3000–25 000 amu and corresponds to helium droplets containing a sodium ion. As can be seen in the lower panel of Fig. 3, the ion-yield spectra for the two mass ranges are very different. While the  $\text{Na}^+\text{He}_m$  exciplex yield decreases with increasing excitation energy, the high mass yield increases noticeably at the ionization threshold. The fact that the low mass ion-yield decreases monotonically implies that highly excited Rydberg states yield no noticeable amounts of  $\text{NaHe}_m$  complexes. A comparison of the high mass ion-yield spectrum to the integrated ZEKE spectrum reveals a perfect agreement between the two spectra. This agreement in combination with the absence of any noticeable  $\text{NaHe}_m$  complexes formation leads us to conclude that the  $\text{Na}^+$  ionic core of the high Rydberg state remains attached to the helium droplets. Based on the experiments we can only speculate on the location of the ionic core. It is energetically favorable for an ion to be located in the interior of the droplets [28,29]. Since the interaction between a  $\text{Na}^+$  ion and a helium droplet is attractive, one expects that a  $\text{Na}^+$  ion initially located on the surface of the droplets dissolves into the droplet. It is, however, not evident that the ionic core of a Rydberg atom will do the same, since the attraction between the ionic core and the helium will be balanced by the repulsive interaction of the orbiting electron with the helium. In light of this, it seems likely that the ionic core is not located at the center of the droplet but resides close to the surface or possibly even on the surface of the droplet. It is this delicate balance that most probably also determines the lifetime of the system, as pointed out by Ancilotto *et al.* [13].

The excitation spectra discussed above have been recorded by monitoring the yield of bare sodium and small  $\text{NaHe}_m$  exciplexes. This in combination with the fact that only ion containing helium droplets are observed above the ionization threshold implies that the Rydberg states of sodium-doped helium droplets with principal quantum number  $n \lesssim 20$  probed in the excitation spectra are not stable on the nanosecond time scale of the laser pulse. Although the lifetime of these states cannot be determined, the intensity distributions of the photoproducts can provide some indications on the variation of the lifetime with principal quantum number. Since the  $\text{NaHe}_m$  exciplex formation is thought to be a sequential process [30], the fact that the yield of the larger  $\text{NaHe}_3$  and  $\text{NaHe}_4$  complexes increases with principal quantum number indicates that atoms excited to higher Rydberg states remain longer on the surface of the droplets. This trend is confirmed by the ZEKE experiments. The lifetime of Rydberg states with

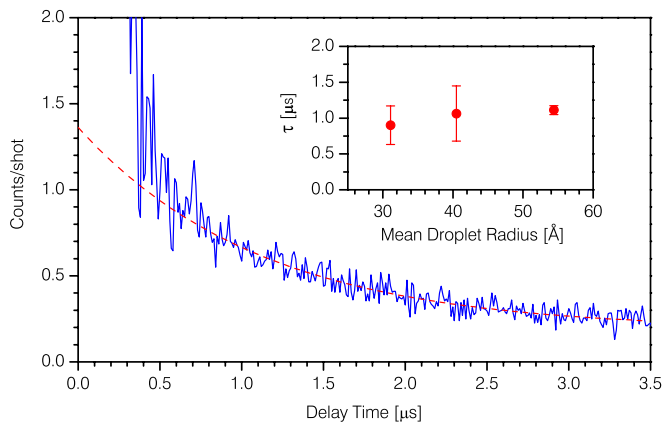


FIG. 4 (color online). Electron yield of sodium-doped helium droplets with a mean radius of  $54 \text{ \AA}$  excited at  $41\,304 \text{ cm}^{-1}$  as function of the time delay between excitation and the ionization by a pulsed electric field of  $5 \text{ V/cm}$ . The data are fitted to an exponential decaying function (dashed line). Inset: Lifetime of the high- $n$  Rydberg states for different droplet sizes.

$n \geq 100$  populated in the ZEKE experiments has been determined by monitoring the electron yield as function of the time delay between the laser excitation and the pulsed field ionization, see Fig. 4. The data have been fitted to an exponential decay to yield a lifetime of  $\tau = 1.1 \pm 0.1 \mu\text{s}$ . The lifetime of these Rydberg states is 3 orders of magnitude longer than that of the lower lying states probed in excitation spectra. However, it is significantly shorter than the lifetime of equivalent states in the free sodium atom [31]. These observations are all in agreement with the suggestion by Ancilotto *et al.* that the lifetime of Rydberg states of the helium droplets is governed by electron-ion recombination [13]. Finally, we would like to remark that the lifetimes of the high- $n$  Rydberg states are independent of droplet size, see inset Fig. 4, which might be expected in view of the large size difference between the droplet and valence electron radii.

Summarizing, we have demonstrated the existence of an unusual type of Rydberg system: a positively charged helium droplet with an orbiting electron. Excitation spectra of sodium-doped helium droplets indicate that this system is not stable on a nanosecond time scale for Rydberg states with principal quantum numbers in the range of  $n = 7\text{--}20$ . ZEKE spectra show that Rydberg states with principal quantum number  $n \geq 100$  are stable and have a microsecond lifetime. Ion-yield spectra indicate that for these high- $n$  Rydberg states the ionic core remains attached to the helium droplet, thereby providing additional evidence for the existence of this exotic Rydberg system. We furthermore found that the ionization threshold of sodium-doped helium is broadened and red-shifted with respect to that of the free atom. These observations could be reproduced within the pseudodiatom model.

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