

# Ultrafast probing of ejection dynamics of Rydberg atoms and molecular fragments from electronically excited helium nanodroplets

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The ejection dynamics of Rydberg atoms and molecular fragments from electronically excited helium nanodroplets are studied with time-resolved extreme ultraviolet ion imaging spectroscopy. At excitation energies of 23.6  $\pm$  0.2 eV, Rydberg atoms in n = 3 and n = 4 states are ejected on different time scales and with significantly different kinetic energy distributions. Specifically, n = 3 Rydberg atoms are ejected with kinetic energies as high as 0.85 eV, but their appearance is delayed by approximately 200 fs. In contrast, n = 4 Rydberg atoms appear within the time resolution of the experiment with considerably lower kinetic energies. Major features in the Rydberg atom kinetic energy distributions for both principal quantum numbers can be described within a simple elastic scattering model of localized perturbed atomic Rydberg atoms that are expelled from the droplet due to their repulsive interaction with the surrounding helium bath. Timedependent kinetic energy distributions of He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> ions are presented that support the formation of molecular ions in an indirect droplet ionization process and the ejection of neutral Rydberg dimers on a similar time scale as the n = 3 Rydberg atoms. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4768422]

#### I. INTRODUCTION

Helium nanodroplets are sub-micrometer scale clusters of superfluid helium that are formed in a supersonic expansion of cryogenically cooled helium gas.<sup>1-4</sup> Their role as a superfluid, cryogenic matrix for electronic, 5-7 vibrational, 3,8,9 and rotational<sup>10,11</sup> spectroscopy of embedded species has led to a steadily growing interest in understanding the fundamental interactions and dynamics inside helium nanodroplets.<sup>9,12</sup> A detailed description of the electronically excited states of helium droplets, all of which lie in the extreme ultraviolet (EUV) region of the electromagnetic spectrum, has proved to be particularly challenging. Synchrotron-based work in the groups of Möller<sup>13</sup> and Toennies<sup>14</sup> paved the way to study these highly excited states and their relaxation pathways. In particular, the observation of discrete fluorescence from desorbed Rydberg atoms and molecules by von Haeften and co-workers unraveled a remarkable cooling mechanism,<sup>15</sup> in which EUV excitation of droplets resulted in localization and ejection of an electronically excited He<sup>\*</sup> atom or He<sub>2</sub><sup>\*</sup> dimer. While photoionization studies of Fröchtenicht et al.<sup>14</sup> and Peterka et al.<sup>16,17</sup> indicated the existence of an indirect ionization channel at excitation energies beyond  $\sim 23$  eV, ejection of electronically excited neutral species is believed to be the dominant de-excitation mechanism of droplets excited below the atomic ionization limit of 24.6 eV.<sup>15,18,19</sup> In this paper, we report time-resolved experiments in order to gain a deeper understanding of the physics that govern the ejection of Ry-dberg atoms and larger fragments from electronically excited helium nanodroplets.

The advent of laser-based femtosecond EUV light sources<sup>20-25</sup> has enabled a new class of experiments to probe the electronic and nuclear dynamics of helium droplets in the time domain.<sup>18, 19, 26</sup> Using femtosecond time-resolved EUV photoelectron imaging. Kornilov et al.<sup>19</sup> identified helium atoms in electronically aligned 1s4p states and unaligned 1s3dstates as the dominant Rydberg fragments after excitation of large ( $\langle N \rangle = 2 \times 10^6$ ) droplets with photon energies of 23.6  $\pm$  0.2 eV. The ejection time scales of atoms in 1s4p states and 1s3d states were determined to be < 120 fs and  $\sim$ 220 fs, respectively. In addition, electron signal at near zero kinetic energy (ZEKE) was observed with a rise time of 2-3 ps. These observations were rationalized within a theoretical model that describes electronically excited droplet states by localized, perturbed atomic Rydberg states. This relatively simple model gives a surprisingly accurate description of the EUV absorption band structure of large helium droplets. An important consequence of the model is that, within a specific band, the excitation energy increases monotonically with increasing depth of the excitation within the droplet surface region. This correlation is supported by the results of an ion imaging study by Bünermann et al.<sup>26</sup> and a theoretical ab initio study of excited states in small helium clusters by Closser and Head-Gordon.<sup>27</sup>

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FIG. 1. Illustration of the femtosecond EUV-pump/IR-probe experiment to monitor the ejection dynamics of Rydberg atoms from electronically excited helium nanodroplets.

In this paper, we report complementary measurements that probe the time-evolving kinetic energy distributions (KEDs) of the Rydberg atoms ejected from He droplets subsequent to EUV excitation. As shown in Figure 1, He droplets are excited with a femtosecond EUV pump pulse centered at 23.6 eV, resulting in ejection of He\* atoms that are ionized with an 800 nm femtosecond probe pulse. Using timeresolved ion imaging techniques, we can thus determine the Rydberg atom abundance and kinetic energy distribution as a function of pump-probe delay. We also present results on the observation of He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> molecular ions.

The experimental results are combined with the findings of a previous femtosecond EUV photoelectron imaging study<sup>19</sup> in order to draw a comprehensive picture of the Rydberg atom ejection mechanism. We find that there are two contributions to the Rydberg atom dynamics: within the cross correlation of the laser pulses,  $He^*(1s4p)$  atoms are ejected from the droplets with low kinetic energies, whereas  $\text{He}^*(1s3d)$  atoms appear on a time scale of 200 fs with considerably higher kinetic energies. These results are explained using a Monte Carlo multiple scattering simulation of the Rydberg atom trajectories in the droplet surface region. The potential energy surfaces for the trajectories are derived from a simplified version of the localized perturbed atomic Rydberg state picture of droplet excitations described in previous work.<sup>19</sup> The overall picture from this analysis is that  $\text{He}^*(1s3d)$  atoms are formed deeper within the droplet than  $\text{He}^*(1s4p)$  atoms. The  $\text{He}^*(1s3d)$  atoms thus experience a greater degree of repulsion with the surrounding He atoms and traverse a larger potential gradient en route to leaving the droplet.

#### **II. EXPERIMENT**

The experiment is described in detail in Refs. 18 and 26. Briefly, the apparatus consists of two major parts: a high harmonic generation beam line to create ultrashort EUV light pulses and a molecular beam instrument equipped with both a photoelectron velocity map imaging spectrometer and an ion imaging spectrometer.

The beam line is driven by a Ti:Sapphire based femtosecond laser system, providing pulses with 25 fs pulse duration, 785 nm central wavelength, and energies up to 5 mJ per pulse at a repetition rate of 3 kHz. The infrared (IR) laser beam is split into two beams. The main part is used to generate high harmonics in a gas cell filled with krypton. Two silicon mirrors placed at Brewster's angle for the fundamental light filter out most of the IR photons while most of the EUV light is reflected. An additional tin filter blocks the remaining IR and suppresses EUV radiation beyond 24 eV. This filter is a crucial component in the setup since it has a major impact on the spectrum of the EUV beam that excites the droplets. Previous measurements were performed using an aluminum filter with a significantly broader transmission window extending far beyond the atomic helium ionization potential of 24.6 eV.<sup>26</sup> The second part of the IR beam is routed through a computercontrolled delay stage. Both beams are combined by means of an annular  $45^{\circ}$  mirror, with the EUV pulse passing through a central hole and the IR light reflected by the mirror. The beams travel collinearly and reflect off a concave multilayer mirror. This mirror fulfills two purposes: its multilayer structure is optimized for reflection of the 15th harmonic at a nominal photon energy of 23.7 eV, and it focuses both beams

into the ion/electron spectrometer where they intersect the helium droplet beam.

The molecular beam instrument consists of a source chamber, a differential pumping stage, and a detection chamber. The beam of helium nanodroplets is created by expanding helium gas under high pressure and low temperatures through a 5  $\mu$ m nozzle into vacuum. In the expansion, the helium cools down further and eventually forms droplets. The droplets then travel through a skimmer into the differential pumping stage and reach the ion/electron spectrometer after passing through a second skimmer. The experiments described here are performed at source conditions of  $T_0 = 13$  K and  $P_0 = 80$  bar leading to an average droplet size of  $\langle N \rangle = 2 \times 10^6$  atoms per droplet.<sup>4</sup>

Both light beams intersect the droplet beam in the interaction volume of a Wiley-McLaren ion time-of-flight (TOF) spectrometer<sup>28</sup> equipped with a time- and position sensitive detector.<sup>29</sup> From the TOF and the detector hit positions, the ion mass, the kinetic energy distribution, and the ion emission angular distribution are derived. Note that this is not a velocity-map imaging experiment;<sup>30</sup> the detector provides position and timing information for each detected ion, from which the ion kinetic energy is directly obtained.

For each pump-probe delay, two measurements are performed, one with both pump and probe beams incident on the target ("pump + probe") and one with the EUV pump beam exclusively ("pump-only"). The IR probe beam alone does not produce any signal. All pump-probe signals presented here are corrected by subtracting pump-only contributions that arise from EUV ionization of the ground state droplets from the pump + probe signals. Each time-delay scan is performed multiple times in alternating directions (increasing and decreasing time delay) to minimize the impact of long term drifts in the experimental setup. The delay step width is 20 fs for scans with 1 ps maximum delay and 0.2 ps for scans with 10 ps maximum delay. Typical data acquisition times are on the order of 3-5 min per data point.

#### III. RESULTS

The time-dependent ion mass spectra consist almost exclusively of monomer, dimer, and trimer ions (Figure 2(a), note the logarithmic scaling of the ordinate). The relative ion yields drop significantly with increasing mass; trimer ions account for less than 5% of the total ion signal. Despite the nominal 24 eV cutoff energy of the tin filter, a small contribution of high energy photons (>24.6 eV) reaches the interaction region, leading to some He<sup>+</sup> background signal in the pumponly spectrum due to direct ionization of helium droplets and helium atoms. This signal does not contribute to the time-dependent data discussed below because the aforementioned correction procedure eliminates signals emerging solely from the EUV pump pulse.

Figure 2(b) shows the predominant partial ion yields as a function of pump-probe delay  $\Delta t$ . The He<sup>+</sup> signal rises within the time resolution of the experiment (120 fs, full-width-athalf-maximum, FWHM), increases during the next ~200 fs, and then remains constant. In contrast, the He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> transients exhibit an instantaneous rise followed by a fast de-



FIG. 2. (a) EUV-pump only mass spectra (solid) and EUV-pump/IR-probe mass spectra recorded at pump-probe time delays of 0.1 ps (open) and 10 ps (striped). (b) Transient partial ion yields of different  $He_N^+$  ions, normalized to the same maximum intensity at 10 ps. Note that some of the data shown in (a) have been published in previous work.<sup>26</sup>

cay within ~200 fs and a subsequent rise on a 2–3 ps time scale. All of these time scales are similar to those previously reported in time-resolved photoelectron spectra of He droplets in the same size range;<sup>19</sup> the instantaneous rise correlates to the appearance of He<sup>\*</sup>(n = 4) Rydberg atoms, the 200 fs time scale corresponds to the decay of the initially excited droplet state and the appearance of He<sup>\*</sup>(n = 3) Rydberg atoms, while the 2-3 ps rise of the He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> ions is close to that of the near ZEKE photoelectron signal. These correspondences are considered in more detail below.

Figures 3(a) and 3(b) show detector hit position distributions of He<sup>+</sup> ions at 100 fs and 10 ps pump-probe delay, respectively. Note the logarithmic scaling of the false color plots. The slightly tilted narrow streaks in the images are residuals of the subtraction procedure that suppresses signals from direct ionization of He background gas along the laser beam path by high energy light leaking through the Sn filter. This signal does not contribute to the pump-probe data presented in the following since the residual consists of both small positive and negative values that average to zero in the analysis. However, the streaks are good indicators for possible



FIG. 3. Detector hit position distributions of He<sup>+</sup> ions at pump-probe delays of (a) 100 fs and (b) 10 ps. The slightly tilted narrow streaks in the images are residuals of the subtraction procedure that suppresses direct ionization signals from He background gas along the laser beam path as indicated on the right. Note the logarithmic scaling of the false color plots.

background contributions from atomic He in our pump-probe data. The background atoms that contribute to the streaks are marked by very low kinetic energies on the order of kT (T  $\approx 200$  K) and therefore spread only very little across the detector during their flight time, leading to a vertical projection of the laser beam onto the ion detector. In contrast, the Rydberg atoms ejected by the droplets have larger kinetic energies, which result in the much broader isotropic distribution of He<sup>+</sup> ions centered on the crossing point between the laser beam and the droplet beam. This distinction confirms that a predominant fraction of the He<sup>+</sup> ions detected in the pump-probe experiment stems from droplets rather than background gas. The different diameters of the isotropic distributions in Figures 3(a) and 3(b) reflect the change of the He<sup>+</sup> kinetic energy distribution as the pump-probe delay is varied. However, the isotropic character of this signal originating from the droplets is maintained at all pump-probe delays.

Figure 4(b) shows KED (vertical axis) of He<sup>+</sup> ions as a function of  $\Delta t$  (horizontal axis). Note that the false color scale is logarithmic. At each time delay, the KED peaks at zero kinetic energy and falls off monotonically toward higher energies. It is readily apparent that the He<sup>+</sup> KED changes significantly with pump-probe time delay. Ions with kinetic energies below  $\sim 150$  meV appear as soon as the pump and probe pulses overlap. Significantly, higher kinetic energies are only observed for delays beyond  $\sim 200$  fs. The black data points in Figures 4(a) and 4(c) are derived by integrating Figure 4(b) over all kinetic energies and all time delays, respectively, and thus represent the total He<sup>+</sup> signal as a function of time,  $I(\Delta t)$ , and the time-integrated KED, P(E), of the He<sup>+</sup> ions. Similar plots for He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> are shown in Figures 5 and 6. Note that the integrated  $I(\Delta t)$  curves from the twodimensional measurements are the same as the time-resolved mass spectra in Figure 2(b), except for different normalizations.



FIG. 4. Time-dependent ion kinetic energy distributions for He<sup>+</sup> (b). The time-dependent He<sup>+</sup> ion intensity  $I(\Delta t)$  ((a) black dotted) is derived by integrating (b) along the kinetic energy axis. The black dotted kinetic energy distribution P(E) in (c) is derived by integrating (b) along the delay axis. The red and green lines in (a) and (c) represent the components *M*1 and *M*2 as described in the text; the gray lines represent the overall fit. Panel (d) shows the two-dimensional fit of the transient ion kinetic energy distributions. Note the logarithmic scale of the false color plots.



FIG. 5. Transient ion kinetic energy distributions for  $He_2^+$  (b). The red, green, and blue lines in (a) and (c) represent the components D1, D2, and D3 as described in the text; the gray lines represent the overall fit. Panel (d) shows the two-dimensional fit of the transient ion kinetic energy distributions. Note the logarithmic scale of the false color plots.

#### **IV. ANALYSIS**

In this section, we focus primarily on the results for the  $He^+$  distributions in Figure 4; analysis of the results for  $He_2^+$ and He<sub>3</sub><sup>+</sup> is then covered briefly. Inspection of the  $I(\Delta t)$  distribution in Figure 4(a) shows a very rapid rise in signal within the first 100 fs followed by a slower rise over several hundred fs, suggesting that at least two processes with different time scales are contributing to the integrated ion signal. Similarly, the P(E) curve in Figure 4(c) appears to comprise two contributions, a narrow low energy feature from 0 to 0.1 eV superimposed on a broader feature extending to 0.85 eV. The origins of these contributions are suggested by the results of our previous time-resolved photoelectron imaging study on He droplets under the same excitation conditions. That work showed that  $\text{He}^*(1s4p)$  Rydberg atoms were ejected from the droplet within the time resolution of the experiment (120 fs FWHM), while  $He^*(1s3d)$  Rydberg atoms were ejected on



FIG. 6. Transient ion kinetic energy distributions for  $He_3^+$  (b). The red and blue lines in (a) and (c) represent the components *T*1 and *T*2 as described in the text; the gray lines represent the overall fit. Panel (d) shows the two-dimensional fit of the transient ion kinetic energy distributions. Note the logarithmic scale of the false color plots.

a time scale of 220 fs. We therefore start out in the analysis based on the assumption that the data in Figure 4 reflect the KED and time-dependent yield of these two He<sup>\*</sup> excited states.

Based on the above considerations, the two-dimensional data set in Figure 4(b) is fit as the sum of two products

$$M(E, \Delta t) = I_{M1}(\Delta t)P_{M1}(E) + I_{M2}(\Delta t)P_{M2}(E).$$
(1)

Here, the  $P_{M1,M2}(E)$  functions are the KEDs of He<sup>\*</sup> atoms with principal quantum numbers n = 4 (M1) and n = 3(M2). These are assumed to be time-independent and only their relative contributions  $I_{M1,M2}(\Delta t)$  change as a function of the pump-probe delay  $\Delta t$ . The time-dependent relative yields  $I_{M1,M2}(\Delta t)$  are expressed as the Heaviside step function  $\theta(\Delta t)$ for n = 4 and an exponentially rising component that appears on a 220 fs time scale for n = 3, leading to

$$M(E, \Delta t) = \theta(\Delta t) P_{M1}(E) + [1 - e^{-\Delta t/220 \ fs}] P_{M2}(E).$$
(2)

The KEDs are derived in a series of least-squares fits using Eq. (2) convoluted with a Gaussian distribution that accounts for the experimental time resolution of 120 fs (FWHM). The two-dimensional data set is divided into narrow (10 meV wide) energy slices:  $M_i(E_i, \Delta t) = M(E_i \le E < E_i)$  $+\delta E, \Delta t$ ,  $\delta E = 10$  meV,  $E_i = i \cdot \delta E$ . The pump-probe signal in each slice is fitted according to Eq. (2), yielding two amplitudes  $P_{M1}(E_i)$  and  $P_{M2}(E_i)$ . The series of amplitudes  $P_{M1}(E_i)$ ,  $P_{M2}(E_i)$  are point-wise representations of the KEDs of the two components  $P_{M1}(E)$  and  $P_{M2}(E)$ , which are plotted as red and green curves, respectively, in Figure 4(c). Correspondingly, the time-dependent functions  $I_{M1}(\Delta t)$  and  $I_{M2}(\Delta t)$ , convoluted with the experimental time resolution, are plotted as the red and green curves, respectively, in Figure 4(a). Figure 4(d) shows the two-dimensional modeling of the data by the fit results. The fit quality is very good. Note that the logarithmic color scale permits to distinguish differences between the data in Figure 4(b) and the two-dimensional fit in Figure 4(d) on a level of a few percent of the maximum intensity.

An alternative fitting procedure in which both relative yields  $I_{M1,M2}(\Delta t)$  are described by exponentially rising contributions  $I_n(\Delta t) = 1 - e^{\Delta t / \tau_n}$  with freely variable rise times  $\tau_n$  leads to similar results (e.g., a 200 ± 40 fs rise time for component M2), but doubling the number of free fit parameters significantly increases the uncertainty of the energy distributions  $P_{M1,M2}(E)$ . In contrast, fixing the time constants to the values derived from our previous photoelectron imaging study<sup>19</sup> leads to well-defined fit results and permits a direct comparison to the corresponding electron measurements.

The accurate description of the entire two-dimensional data set in Figure 4(b) by only two components that follow the dynamic trends of the 1s3d and 1s4p ionization signals observed in the photoelectron imaging experiment indicates that the *ad hoc* defined fit functions  $P_{M1}(E)$  and  $P_{M2}(E)$  are faithful representations of the KEDs of neutral atoms ejected in 1s4p and 1s3d Rydberg states, respectively. This assertion is supported by a comparison of the time-dependent electron and ion yields shown in Figure 7. Figure 7(a) compares



FIG. 7. Comparison of electron and ion signals. (a) Electron (red) and ion channels with 220 fs rise time, (b) electron (red) and ion channels that rise instantly. M1 and M2 are the two components of the He<sup>+</sup> signal as shown in Figure 4(a). Electron and ion signals are normalized to the total electron signal and the total ion signal, respectively.

the 1s3d photoelectron signal (red) with the ion yield curve  $I_{M2}(\Delta t)$  (black dashed). Figure 7(b) compares the 1s4p photoelectron signal (red) and the ion yield curve  $I_{M1}(\Delta t)$  (black dashed). We emphasize that the relative scaling of the electron and ion curves in Figure 7 is not adjusted to match their amplitudes. Instead, all electron and ion signals are scaled by a single factor that is derived by matching the total electron yield with the total ion yield at a pump-probe time delay of 9 ps. The quantitative agreement between the electron and ion signals the direct correlation between the electron and ion measurements outlined above.

Note that at long times, the sum of the two He<sup>+</sup> (dashed) curves in Fig. 7(a) is less than unity since the normalization factor is derived from the signals of all ions, including dimers and trimers. Similarly, the electron (red curves) normalization factor is derived from all electrons, including all photoelectrons that are associated with excited droplet states. The curves agree with respect to the ratio of M1 and M2 and they agree with respect to the ratio of both signals relative to all other signals detected in the experiment.

The two-dimensional distributions for  $He_2^+$  and  $He_3^+$  can be similarly decomposed into products of onedimensional distributions as in Eq. (1). We find that three terms and two terms, respectively, are needed to describe the dimer (D) and trimer (T) results

$$D(E, \Delta t) = e^{-\Delta t/\tau_1} P_{D1}(E) + (1 - e^{-\Delta t/\tau_1}) P_{D2}(E) + (1 - e^{-\Delta t/\tau_2}) P_{D3}(E),$$
(3)

$$T(E, \Delta t) = e^{-\Delta t/\tau_1} P_{T1}(E) + (1 - e^{-\Delta t/\tau_2}) P_{T2}(E).$$
(4)

Fits were performed under the constraints that  $\tau_1$  was set to  $\tau_1 = 220$  fs and that  $\tau_2$  is the same for dimer and trimer ions. The reasoning behind these constraints is that both electron and ion data should display the same dynamic trends and that the interpretation of a fit procedure is increasingly reliable for a decreasing number of free fit parameters. This procedure resulted in  $\tau_2 = 2.5$  ps and the P(E) curves shown in Figures 5(c) and 6(c).

#### V. DISCUSSION

#### A. Modeling the Rydberg atom ejection mechanism: Coupling of electronic excitation and nuclear motion

In the following, a microscopic description of the Rydberg atom emission is presented that correctly predicts the major features of the monomer ion KEDs. The description is based on a model that assigns excited droplet states below 24 eV to perturbed atomic Rydberg states located in the droplet surface region. The model is described in detail by Kornilov et al.<sup>19</sup> Briefly, the energies of atomic Rydberg states embedded in the droplet are approximated by the eigenvalues of a model hamiltonian with a potential that consists of the Coulomb potential of the ionic core of the Rydberg state plus a step function that represents the average influence of the droplet environment on the Rydberg electron. The distance of the barrier from the ionic core is approximated by the nearest neighbor distribution inside the droplet.<sup>17</sup> The barrier height is estimated to scale linearly with the local density surrounding the Rydberg atom, ranging from 0 eV in the free atom limit of the outermost surface regions to 1 eV in the droplet bulk; the latter value corresponds to the energy of a free electron in liquid He relative to the vacuum.<sup>31</sup>

The resulting potential is described by

$$V(r, R) = -\frac{1}{r} + V_0(R)\theta(r - r_{nn}),$$
 (5)

where  $V_0(R) = 1$  eV ×  $\rho(R) / \rho_{bulk}$  is the barrier height as a function of the local density  $\rho(R)$  at a distance *R* of the ionic core from the droplet center, *r* is the distance between the Rydberg electron and the ionic core,  $r_{nn}$  is the nearest neighbor distance, and  $\theta(r-r_{nn})$  is the Heaviside step function. The original model<sup>19</sup> employed cylindrically symmetric potentials to account for the local density variations within the spatial extent of a single Rydberg atom. Here, we apply a simplified version that assumes spherically symmetric potentials for the description of the localized Rydberg excitations as described by Eq. (5). This choice was made because simulations of the KEDs using the cylindrically symmetric potentials resulted in considerably poorer agreement with experiment, as discussed in more detail in Sec. V C.

The potential energy curves of atomic 1s3p and 1s4p Rydberg states derived from solving the Schrödinger equation with a model potential according to Eq. (5) are illustrated in Figure 8. The local density of the droplet environment varies between 10% and 90% of the bulk density within a 6 Å thick surface region, centered around the nominal droplet radius of 280 Å.<sup>32</sup> The density-dependent barrier height of the model potential leads to a corresponding blueshift of the perturbed Rydberg states. The gray band in Figure 8 indicates the energy range of the pump pulse. The overlap of the gray band with the Rydberg energy curves indicates that in the current experiment, excitation leads either to weakly perturbed 1s4pstates in the outermost range of the droplet surface or to more strongly perturbed 1s3p states in the inner surface region and, possibly, within the droplet interior.

The depth-dependent blueshifts of the atomic Rydberg states in the narrow surface region result in a steep potential energy gradient, i.e., a force that drives the excited atoms out



FIG. 8. Calculated blueshift of atomic 1s3p and 1s4p states in the surface region of a droplet containing  $2 \times 10^6$  atoms, using Eq. (5) in text. The gray shaded area marks the spectral range covered by the pump pulse. The vertical dashed line indicates the nominal droplet radius.

of the droplet. This mechanism converts the electronic energy of the blueshifted, perturbed Rydberg states into kinetic energy of the ejected Rydberg atoms. A simple adiabatic picture in which the principal quantum number of the excitation in the droplet is the same as that of the correlated desorbed Rydberg atom then readily explains the significant difference between the two KEDs in Figure 4(c). The strongly blueshifted Rydberg excitations in the n = 3 manifold can release significantly more kinetic energy into the associated 1s3d fragment atoms than the weakly perturbed n = 4 excitations into the associated 1s4p fragments. However, it takes longer for the n = 3 fragments to be detectable outside the droplet due to their transit through the surface region. The potentials in Figure 8 thus explain why the n = 3 fragments with higher kinetic energies emerge later from the droplet than the n = 4 fragments with lower kinetic energies.

We note that according to Fig. 8, n = 3 fragments can be formed over a range of distances from the droplet surface, emerging from the droplets at different times and with different kinetic energies. While this might result in a timedependent kinetic energy distribution for this channel, we see no evidence for such an effect in our experimental results, which are fit well with the time-independent KEDs described in Sec. IV.

### B. Monte Carlo simulations of Rydberg atom trajectories

A more quantitative description of the Rydberg atom desorption is obtained by a Monte Carlo simulation of Rydberg atom trajectories along the potential energy surfaces illustrated in Figure 8. Elastic scattering with surrounding helium atoms during the trajectories is taken into account within a simple hard sphere scattering approximation. The scattering probability is calculated based on the local density profile<sup>32</sup> and scattering cross sections that are estimated by the nominal geometric cross sections of He atoms: 0.30 Å<sup>2</sup>, 71 Å<sup>2</sup>, 230 Å<sup>2</sup>, for atoms in He(1*s*<sup>2</sup>), He(1*s*3*p*), and He(1*s*4*p*) states, respectively.<sup>33,34</sup> For every starting position, numerous trajectories are modeled. The results are weighted with the pump pulse spectrum and convoluted with the droplet size distribution.<sup>35</sup> Note that the differentiation between excitation of perturbed 1*s*3*p* states and ejection of 1*s*3*d* states as



FIG. 9. Comparison of simulated (red) and measured (black) kinetic energy distributions of He\*(1*snp*) Rydberg atoms with principal quantum numbers (a) n = 4 and (b) n = 3 ejected by helium droplets. The gray lines represent simulated distributions when scattering is neglected.

discussed previously<sup>19</sup> has no impact here within the precision of the measurements and model calculations.

Figure 9 shows the simulated KEDs in red for both the n = 4 (Figure 9(a)) and n = 3 (Figure 9(b)) Rydberg atoms in comparison to the measured distributions  $P_{M1,M2}(E)$  (black). Both measured distributions, which differ significantly for n= 4 and n = 3 states, are reproduced by the model calculation for kinetic energies above  $\sim 100$  meV. The impact of elastic scattering on the KEDs is demonstrated by the gray curves in Figure 9, which show the calculated KEDs when scattering is neglected. In particular, the predicted average kinetic energy of the n = 3 fragments would be off by about a factor of two compared to the measurements if elastic scattering were neglected. The significantly reduced impact of scattering on the n = 4 KED compared to the n = 3 KED reflects the lower average scattering probability for the n = 4 fragments that emerge from the outermost surface regions as opposed to the n = 3 fragments that emerge from a greater depth. The overall amplitudes of the simulated curves are arbitrary since the absolute photoabsorption cross sections in the experiments are unknown. The simulated curves have been scaled for best agreement with the measured spectra. Curves that represent calculations with and without the inclusion of elastic scattering have been scaled to the same integrated intensity for each principal quantum number.

Note that the experiment probes the asymptotic KEDs of monomer fragments after their ejection from the droplet. It cannot directly access the dynamics inside the droplet that lead to the asymptotic distributions. If the Rydberg atoms are ionized by the probe pulse while they are still inside the droplet, the interaction of the resulting helium ion with surrounding ground state atoms leads to the formation of larger ionic fragments as has been pointed out by several groups.<sup>14, 26, 36–38</sup> The dimer and trimer results presented here support this picture as discussed below. Therefore, while our Monte Carlo simulation includes a time-dependent evolution

of the monomer KEDs inside the droplet, all experimentally accessible distributions presented in Figures 4 and 9 are compared to the time-independent, asymptotic KEDs that emerge from the simulation after the Rydberg atom has left the droplet.

## C. Limitations of the model and comparison to related studies

The experimental and calculated KEDs differ substantially for kinetic energies below  $\sim 100$  meV. The experimental distributions for the n = 3 and n = 4 KEDs exhibit an additional peak at < 10 meV that is not reproduced within the presented model. The low energy peak in the n = 4 KED may result in part from residual helium atoms in the experimental chamber. However, there should be no corresponding contribution to the KED for the n = 3 state since the 1s3p state of free helium atoms is not excited by the pump pulse.<sup>19</sup> Furthermore, the n = 3 component (M2) is associated with a  $\sim 220$ fs rise time while free helium atoms lead to a step-function like onset of the pump-probe ionization signal.<sup>18,39</sup> At least some of the low kinetic energy contributions in Figure 9 that are not captured by the model calculations are therefore most likely caused by mechanisms that are not included in the multiple scattering calculation. Possible processes include inelastic and multi-atom collisions involving attractive potential curves of electronically excited helium molecules and clusters. A quantitative modeling of these dynamics, however, is beyond the scope of this work.

We also tried to simulate KEDs based on adiabatic dynamics along electronic surfaces that were derived from a cylindrically symmetric local potential as described in our previous work.<sup>19</sup> The resulting KEDs are dominated by artifacts and do not reproduce the measurements. For example, the state that asymptotically correlates to the atomic He(4*s*) state leads to a sharp KED peak centered at 60 meV that is not reproduced by the data. A more sophisticated description including non-adiabatic dynamics that account for the coupling between different potential energy surfaces may improve the situation. However, we note that model calculations of local Rydberg excitations based on spherically symmetric potentials reproduce the measured fluorescence excitation spectra of Möller and co-workers<sup>13</sup> equally well as calculations based on cylindrically symmetric potentials.<sup>19</sup>

It is of interest to compare the physics of Rydberg atom ejection as revealed in this study to that of desorption of electronically excited alkali atoms from helium droplets that has been studied by other groups.<sup>40–43</sup> As discussed in Sec. III, the He<sup>+</sup> ion signal from ionization of ejected He<sup>\*</sup> states is isotropic (Fig. 3), a result that contrasts with the anisotropic angular distributions seen for alkali atoms.<sup>40–42</sup> Alkali atoms reside in surface dimples, i.e., local depressions in the droplet surface, leading to a well-defined equilibrium distance of the dopant relative to the droplet surface and vanishing overlap between the density profiles of the dopant and the helium atoms.<sup>42,44,45</sup> This arrangement lends itself to an effective two-center, or pseudo-diatomic model in which the alkali atom experiences the average effect of all helium atoms as that of a second pseudo-atom.<sup>40,43,44,46</sup> In this model, the angular momentum component ( $\Lambda$ ) along the symmetry axis of the system is a good quantum number in the ground and excited states of the doped droplet, leading to energy splittings between states with different values of  $\Lambda$  that can be experimentally resolved. Just as in diatomic molecules,<sup>47</sup> there can be a preference for exciting a droplet with its symmetry axis either parallel or perpendicular to the laser polarization direction, depending on  $\Delta\Lambda$  for the transition in question. The subsequent fast desorption of alkali atoms along the surface normal with negligible scattering on surrounding helium atoms can then lead to highly anisotropic photofragment angular distributions.<sup>40–42</sup>

The physical picture in the experiment on pure droplets is very different, since there is no corresponding axis of symmetry. The He<sup>\*</sup>(4*p*) atoms are ejected from the droplet with an isotropic angular distribution but an aligned electronic distribution, as revealed by the photoelectron angular distribution from these fragments observed in our previous work.<sup>19</sup> These results are consistent with the initial VUV excitation being strongly localized on one or a small number of He atoms at the droplet surface, with the excitation probability of a particular surface atom being independent of its position. The resulting  $\text{He}^*(4p)$  atom experiences only a mild repulsion with the droplet, as indicated in Fig. 8, and leaves the droplet while retaining the degree of electronic alignment similar to that seen for the analogous excitation of an isolated He atom. The  $\text{He}^{*}(3d)$  atoms are also ejected isotropically, but show no electronic alignment, as expected for a stronger interaction with the droplet environment and consistent with our picture that these fragments result from excitation within the droplet (but still near the surface). The exact nature of the excitation leading to formation of these fragments is still an open question, however.

#### D. Dimer and trimer ions

The dynamics that underlie the He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> signals are still under consideration. It is likely that the component of the He<sub>2</sub><sup>+</sup> signal that exhibits a rise time of  $\tau_1 = 220$  fs (green curves in Figures 5(a) and 5(c)) results from ejection of He<sub>2</sub><sup>\*</sup> from the droplet that is ionized by the probe pulse, given the similarity with the atomic He<sup>\*</sup>(n = 3) signal in Figure 4. The signal decaying on a  $\tau_1 = 220$  fs time scale may be due to ionization of excited Rydberg atoms while they are still within the surface region of the droplet. This assertion is supported by the observation of an isotropically emitted photoelectron signal that decays on the same time scale and that has previously been associated with ionization of excited droplets by the probe pulse.<sup>19</sup>

It is striking that the rise time  $\tau_2 = 2.5$  ps for the slowest components of the He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> signals is similar to that for the ZEKE photoelectron signal seen in our earlier work.<sup>19</sup> Although the origin of the ZEKE signal is still under discussion, it most likely results from autoionization within the droplet or from electronically excited smaller clusters ejected from the droplet. The slowly rising components of the He<sub>2</sub><sup>+</sup> and He<sub>3</sub><sup>+</sup> signals would then correspond to ionic species whose formation accompanies autoionization.

#### **VI. CONCLUSIONS**

Ultrafast ejection dynamics of helium Rydberg atoms with principal quantum numbers n = 3, 4 from electronically excited helium nanodroplets are studied by femtosecond time-resolved EUV ion imaging. Comparison to previous time-resolved photoelectron spectra confirms that atoms in different Rydberg states are ejected on different time scales and with different kinetic energies. While atoms in n = 4states separate from the droplet within less than 120 fs and with kinetic energies below 200 meV, atoms in n = 3 states are ejected within 220 fs and with kinetic energies up to 850 meV. The correlation between the quantum-state dependent ejection time scales and kinetic energy distributions is explained within a model that describes electronically excited droplet states within a picture of localized atomic Rydberg states whose energies are blueshifted by their interaction with the surrounding helium bath. Within this model, the helium density gradient in the droplet surface region leads to a corresponding potential energy gradient that drives the excited atoms out of the cluster. Monte Carlo simulations of n = 3, 4 Rydberg atom trajectories based on this model reproduce major parts of the kinetic energy distributions for both principal quantum numbers. Some very low kinetic energy contributions are not captured by the model and are tentatively assigned to inelastic and multi-atom collisions involving attractive potential curves of electronically excited helium molecules and clusters.

Time-dependent  $\text{He}_2^+$  and  $\text{He}_3^+$  kinetic energy distributions indicate that dimer and trimer fragments are produced in a variety of processes. A previously observed indirect ionization process is likely linked to the formation of both dimer and trimer ions. Excited neutral dimers may be ejected on a similar time scale as n = 3 atoms. Generally, trimer ions carry less than half the kinetic energy of dimer ions. For each type of fragment, however, different formation processes lead to similar kinetic energy distributions.

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