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Spectroscopy and dynamics of barium-doped helium nanodroplets

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Excitation spectra up to the ionization threshold are reported for barium atoms located on the surface of helium nanodroplets. For states with low principal quantum number, the resonances are substantially broadened and shifted towards higher energy with respect to the gas phase. This has been attributed to the repulsive interaction of the excited atom with the helium at the Franck-Condon region. In contrast, for states with high principal quantum number the resonances are narrower and shifted towards lower energies. Photoelectron and ZEKE spectroscopy reveal that the redshift results from a lowering of the ionization threshold due to polarization of the helium by the barium ionic core. As a result of the repulsive interaction with the helium, excited barium atoms desorb from the surface of the droplets. Only when excited to the $6s6p\ ^1P_1$ state, which reveals an attractive interaction with the helium, the atoms remain attached to the droplets. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3701565>]

I. INTRODUCTION

Helium nanodroplets are considered an ideal spectroscopic matrix due to their high cooling rate, low temperature, and weak interactions.^{1–3} As a result, helium droplets are nowadays routinely used for the spectroscopic characterization of molecules. At the same time, the properties of helium droplets themselves are investigated by spectroscopic means. Alkali atoms play an important role in this respect as they are one of the few species known to reside on the surface of the helium droplets and thus able to probe the boundary region.⁴ Consequently, the $np\ ^2P \leftarrow ns\ ^2S$ transitions of alkali atoms attached to helium nanodroplets have been extensively investigated both experimentally and theoretically, see, e.g., Refs. 5–9 and references therein. Recently, transitions involving higher excited states have been explored as well.^{10–15} From these studies some general trends could be identified. The spectra involving states with low and intermediate principal quantum number are characterized by broad resonances that are blue-shifted with respect to the corresponding atomic resonances. This reflects the repulsive interaction of the excited valence electron of the atom with the helium. For states with large principal quantum number where the mean radius of the electron orbit is comparable or larger than the size of the droplet, the interaction of the valence electron with the helium decreases and a Rydberg-like system results.^{10,14,16} In addition to the spectroscopy, the dynamics of excited alkali atoms has been investigated.^{6,7,17–21} It was found that excited atoms desorb from the droplets on a picosecond time scale, either as bare atoms or as alkali-helium exciplexes depending on the energy of the exciting photon.^{5,7,10–12,17} The heavy alkalis, rubidium, and cesium form an exception as they remain attached to the droplet when excited close to the gas phase D1 transition.^{14,22}

In contrast to the alkalis, the spectroscopy and dynamics of alkaline earth atoms attached to helium droplets is much less well characterized, even though these systems have been extensively used as spectroscopic probes of superfluid and solid helium.^{23–31} First spectra of the $nsnp\ ^1P_1 \leftarrow ns^2\ ^1S_0$ transitions of alkaline earth atoms attached to helium nanodroplets have been recorded using laser-induced fluorescence spectroscopy.^{32–34} As the resonances in the spectra of Ca, Sr, and Ba all were noticeably narrower than the corresponding transitions in bulk helium, it was concluded that these atoms reside on the surface of the droplets. In contrast, the spectrum of Mg resembled strongly that recorded in bulk helium, from which it was concluded that Mg resides in the interior of helium clusters. More recent spectroscopic and mass spectrometric experiments have questioned the interior location of the Mg,^{35,36} which has sparked intense theoretical effort to determine the location of the alkaline-earth atoms.^{37–41} It was theoretically found that while the light alkaline-earth atoms Be and Mg are solvated by the helium, the heavier Ca, Sr, and Ba atoms reside on the surface in a dimple-like structure that is significantly deeper than for the alkali atoms. It is *a priori* not clear what the effect of the more pronounced dimple structure is on the absorption spectra involving higher excited states or on the dynamics of the excited atoms. To address these questions, we have performed an extensive study of barium doped helium droplets using a variety of spectroscopic techniques. More specifically, we address here the dynamics of the barium atom following excitation via the $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ and $6s6d\ ^1D_2 \leftarrow 6s^2\ ^1S_0$ transitions, the spectroscopy of excited states up to the ionization threshold, and the ionization dynamics of barium-doped helium droplets.

II. EXPERIMENTAL SETUP

The experimental setup has been described in detail before.^{42,43} In brief, helium droplets consisting on average

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of several thousand atoms are formed by expanding high-purity ^4He gas at a pressure of 30 bar into vacuum through a $5\text{ }\mu\text{m}$ orifice cooled to cryogenic temperatures by a closed cycle refrigerator. By adjusting the temperature of the nozzle the average droplet size can be systematically varied.^{44–46} After passing a skimmer, the droplets pick up barium atoms as they traverse an oven containing barium metal. The temperature of the oven is adjusted to ensure that the droplets on average pick up less than one Ba atom. Via a differential pumping stage the doped droplets enter a vacuum chamber holding a velocity map imaging setup. At the center of the setup, the barium-doped droplets are excited by crossing the droplet beam perpendicularly with the output of a Nd:YAG pumped dye laser. The laser system is operated at a repetition frequency of 20 Hz and provides radiation with a linewidth of less than 0.1 cm^{-1} and a pulse energy in the range of 5–25 mJ. Following excitation, the barium atoms are ionized by the absorption of an additional photon from either the same laser pulse or that of another dye laser synchronized to the excitation laser. The ions, or alternatively the photoelectrons, are accelerated by the applied electric fields and projected onto a position sensitive detector consisting of a pair of microchannel plates (MCP) and a phosphor screen. The light emitted by the phosphor screen is imaged onto a high-resolution CCD camera that is read out after every laser shot. The individual images are analyzed online and the centroids of the impacts are determined. The kinetic energy distributions are determined by performing an inverse Abel transform on the image constructed from the accumulated centroids. Alternatively, excitation spectra are recorded by monitoring the number of impacts on the detector as a function of laser frequency. Both the ion images and the spectra can be recorded at a specific mass or mass range by gating the front of the detector at the arrival time of the ions of interest. By using the setup in a different mode of operation it is also possible to record zero kinetic energy (ZEKE) spectra with a resolution of 4 cm^{-1} .⁴³

III. RESULTS

A. Ba(6s6p)

1. Excitation spectrum

Both theory and experiment indicate that barium atoms are located on the surface of helium droplets.^{33,38} Hence, excitation of the barium can lead to the desorption of the atom from the droplet. This allows recording excitation spectra with high sensitivity, as has been shown for alkali atoms.^{10,11} Following excitation, the atoms are ionized by the absorption of an additional photon. Spectra are then recorded by monitoring the yield of bare barium ions as function of excitation frequency. In case of barium, the photon energy for excitation of the $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ transition is insufficient to ionize the excited atom by the absorption of a second photon.⁴⁷ We therefore have applied a $1+1'$ excitation scheme, using a photon energy of $24\,155\text{ cm}^{-1}$ for the ionization. At this frequency very little excess energy is deposited upon ionization which allows recording high resolution photoelectron spectra via the $6s6p\ ^1P_1$ state, *vide infra*. The excitation spectrum

FIG. 1. $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ excitation spectrum of barium attached to helium droplets with a mean radius of $41\text{ }\text{\AA}$, recorded by monitoring the yield of Ba^+ (upper panel), BaHe_n^+ complexes with $n = 10^2\text{--}10^4$ (middle panel), and photoelectrons (lower panel). The spectra are recorded using a $1+1'$ excitation scheme with the ionizing photon having an energy of $24\,155\text{ cm}^{-1}$. The lower panel also shows the calculated spectrum based on the pseudo-diatomic model. The corresponding transition in the free barium atom is indicated by an asterisk.

recorded this way is presented in the upper panel of Figure 1. It strongly resembles the spectrum recorded by Stienkemeier *et al.* using laser-induced fluorescence,³³ indicating that both detection schemes probe the same excited states. It should be noted that the signal levels observed in the present study are almost two order of magnitude lower than in the work on sodium-doped helium droplets which employed the same detection scheme.¹¹ This could be an indication that the excited barium atoms do not desorb but remain attached to the droplets.

In order to test this hypothesis we have recorded time-of-flight mass spectra. The mass spectrum recorded following excitation at $18\,120\text{ cm}^{-1}$, corresponding to the maximum of the absorption band, and subsequent ionization by the absorption of a $24\,155\text{ cm}^{-1}$ photon is shown in Figure 2. It reveals not only the presence of bare barium ions but also of Ba^+He_n complexes. Individual complexes up to $n = 200$ can be identified in the spectrum. Closer inspection of the spectrum reveals also the presence of ionic species in the 10^4 mass range, corresponding to helium droplets containing a barium ion. The lower panel of Figure 2 shows a detailed view of the high mass part of the spectrum which is now plotted as the number of helium atoms. This mass spectrum resembles those recorded for other systems.^{43,48} Like those mass spectra, the spectrum presented here deviates from the expected log-normal distribution having a mean droplet size of 6080 helium atoms.^{44,46} This deviation, especially the dip in the center of the

FIG. 2. TOF mass-spectrum of barium-doped helium nanodroplets with an estimated mean radius of 41 Å (corresponding to 6080 helium atoms) recorded following excitation of the $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ transition at $18\,120\text{ cm}^{-1}$ and subsequent ionization by the absorption of a $24\,155\text{ cm}^{-1}$ photon. Top panel: overview of the full mass spectrum. The inset shows the progression of Ba^+He_n complexes. Bottom panel: high masses region of the spectrum converted to the number of ^4He atoms. Each data point is a sum of over 128 adjacent data points shown in the upper panel.

distribution, can be attributed to the initial velocity of the ions parallel to the detector surface in combination with a spatial variation of the sensitivity of the microchannel plate detector. Since the high mass signal is only observed if both lasers are present, we conclude that a fraction of the excited atoms remains attached to the helium droplets. Unfortunately, it is not possible to quantify this fraction from the observed intensity ratios in the mass spectrum due to the strong mass dependence of the detection efficiency of the MCP.

As the spectrum presented in Figure 1 is an action spectrum, it is not evident that it corresponds to the absorption spectrum of the system. For alkalis, for example, it has been found that the spectra depend strongly on the type of ion that is being detected.^{11,19,49} We therefore have also recorded spectra by monitoring the yield of large Ba^+He_n ($250 < n < 10\,000$) complexes, see middle panel of Figure 1. This spectrum is identical to that recorded by monitoring the barium ion yield, suggesting that the spectra correspond to the absorption spectrum. Additional evidence is provided by the spectrum recorded by monitoring the electron yield which is presented in the lower panel of Figure 1. Since the photoelectron yield is not noticeably affected by the helium, this spectrum will resemble most closely the absorption spectrum.⁵⁰

Excitation spectra of the $np\ ^2P \leftarrow ns\ ^2S$ transition in alkali-doped helium droplets have been successfully reproduced using the so-called pseudo-diatomic model.⁵ In this

model, the internal degrees of freedom of the helium droplet are ignored, and the system is treated as a diatomic molecule in which the helium droplet plays the role of the second atom. The interaction between the alkali atom and the helium droplet is reduced to a one-dimensional potential, which as a first approximation can be calculated as the sum of alkali-He pair potentials. For higher excited states, a more sophisticated method is required that takes into account helium-induced configuration mixing.^{11,51} The absorption spectrum of barium attached to helium droplets has been simulated with this pseudo-diatomic approach. The ground state interaction potentials for droplets consisting of 1000, 2000, and 3000 helium atoms have been calculated using the $\text{Ba}(6s^2\ ^1S_0)$ -He pair potential of Lovallo and Klobukowski⁵² and the helium density profiles computed by Barranco and co-workers.³⁸ The excited state interaction potentials have been determined within the Franck-Condon approximation using the $\text{Ba}(6s6p\ ^1P_1)$ -He pseudo-potentials of Czuchaj *et al.*⁵³ In these calculations, the orientation of the electron orbital with respect to the symmetry axis of the system, defined by the barium atom and the center of the droplet, has been explicitly taken into account.⁸ The interaction potentials for BaHe_{3000} are shown in Figure 3 as function of the distance between the barium atom and the center of the droplet, z . The potential curves are labeled according to the correlating atomic states and the value of Λ , being the projection of the electron's orbital angular momentum onto symmetry axis of the system, i.e., Σ for $\Lambda = 0$ and Π for $\Lambda = 1$. All three potential curves show a clear minimum. The binding energy of ground state barium to the helium droplet is 42 cm^{-1} , while that for excited barium is 47 and 19 cm^{-1} for the Σ and Π state, respectively. This indicates that upon excitation the barium atom may well remain attached to the helium droplet. At the equilibrium distance of the ground state, $z = 33.5\text{ Å}$, both excited state potentials are repulsive and consequently the excitation spectrum will be characterized by bound-free transitions. The excitation spectrum has been calculated as the Franck-Condon factors for transitions from the lowest vibronic state to the repulsive excited states using the BCONT 2.2 program of Le Roy.⁵⁴ The theoretical spectrum, shown in the lower panel of Figure 1, is shifted noticeably towards higher frequencies compared to the transition in the free atom, in agreement with experiment. The width of the calculated spectrum is considerably narrower than observed experimentally. This difference could be related to the quality of the pair potentials, but could also be due to fact that helium surface fluctuations, which have been shown to lead to a substantial broadening of spectra,⁹ are not taken into account in the present calculations.

2. Photoelectron and ZEKE spectra

Insight into the dynamics following the excitation of the barium can be obtained by photoelectron spectroscopy.^{11,43} Figure 4 shows photoelectron spectra of Ba-doped helium droplets of two different sizes. The spectra have been recorded via a $1+1'$ detection scheme. The system is first excited at $18\,120\text{ cm}^{-1}$, corresponding to the maximum of the absorption spectrum, and subsequently ionized using a $24\,155\text{ cm}^{-1}$

FIG. 3. Effective interaction potentials for $\text{Ba}(6s^2 \ ^1S_0)\text{-He}_{3000}$, $\text{Ba}(6s6p \ ^1P_1)\text{-He}_{3000}$ and $\text{Ba}^+(6s \ ^2S_{1/2})\text{-He}_{3000}$ calculated as the sum of the pair potentials over the ground state helium density profile. The blue band indicates the Franck-Condon region for transitions from the ground state, while the red band indicates the Franck-Condon region for excitation from the $6s6p \ ^1P_1$ at the ground state helium configuration, thus not taking into account the rearrangement of the helium after excitation of the barium atom. The arrow schematically indicates the relaxation of the system after excitation to the $6s6p \ ^1P_1$ states at the Franck-Condon region.

photon. For comparison, also the photoelectron spectrum of free barium recorded via excitation of the $6s6p \ ^1P_1 \leftarrow 6s^2 \ ^1S_0$ transition at $18\,060 \text{ cm}^{-1}$ is shown in Figure 4. The width of this transition is limited by the experimental resolution of the setup. The helium droplet spectra show a similar width but are noticeably shifted towards higher kinetic energies compared to the free atom. This shift appears to be droplet size dependent. Figure 5 shows the variation of the shifts for a wide range of droplet sizes. A similar droplet size dependence has been observed in the photoelectron spectra of other systems and attributed to a lowering of the chromophore's ionization threshold due to polarization of the surrounding helium.^{10,43,50} As the contribution of free barium to the photoelectron spectra is negligible, these spectra provide clear evidence that the majority of barium atoms remains attached to the droplets following excitation to the $6s6p \ ^1P_1$ state.

Photoelectron spectra have also been recorded at other frequencies within the absorption band. These spectra are identical to those reported in Figure 4. This signifies that the system has relaxed on a (sub)nanosecond timescale to a stable configuration before the absorption of the ionizing photon. It should be noted that this configuration does not correspond to the minimum in the excited state interaction potential curves presented in Figure 3. These curves have been calcu-

FIG. 4. The two-color photoelectron (upper panel) and ZEKE (lower panel) spectra of barium-doped helium nanodroplets of different sizes recorded following excitation $6s6p \ ^1P_1 \leftarrow 6s^2 \ ^1S_0$ transition at $18\,120 \text{ cm}^{-1}$. The spectra for the free Ba atom have been recorded at an excitation frequency of $18\,060 \text{ cm}^{-1}$. The photoelectron spectra have been recorded using a photon energy of $25\,155 \text{ cm}^{-1}$ for ionization.

lated within the Franck-Condon approximation, i.e., using the state helium density profile associated with ground state barium. As such they do not include the rearrangement of the helium associated with the relaxation of the system to a new minimum energy configuration.

More detailed information on the desorption probability of the excited atoms can be obtained by ZEKE spectroscopy, which offers a much higher resolution than photoelectron

FIG. 5. Shift of ionization threshold of Ba-doped helium nanodroplets with respect to the threshold of free Ba atoms, $\Delta IT = IT_{Ba} - IT_{BaHeN}$, as determined by photoelectron and ZEKE spectroscopy via $6s6p \ ^1P_1$ excited and the $6s^2 \ ^1S_0$ ground state. The shifts as calculated within the pseudo-diatomic model correspond to ionization from the ground state.

spectroscopy. ZEKE spectra have been recorded by scanning the frequency of the second laser over the ionization threshold after excitation of barium-doped droplets at fixed frequencies within the absorption band. The lower panel of Figure 4 shows ZEKE spectra recorded at an excitation frequency of $18\,120\text{ cm}^{-1}$. For comparison also the ZEKE spectrum of free barium is shown. In agreement with the photoelectron spectra, the ZEKE spectra reveal a droplet size dependent shift which is independent of the excitation frequency. The shifts are reported in Figure 5 and show an excellent agreement with those determined by photoelectron spectroscopy. Additionally, we find that the ZEKE spectra of barium attached to helium droplets are significantly broader than that of the free atom. The lineshape can be described by a Gaussian distribution with a width of $47 \pm 3\text{ cm}^{-1}$ (FWHM). A similar lineshape has been observed in the direct ionization of Na-doped helium droplets and has been attributed to the delocalization of the sodium atom on the surface of the helium droplet.¹⁰ In addition, the broad droplet size distribution is expected to contribute to the linewidth, since the ionization threshold depends on droplet size. Assuming a log-normal droplet size distribution⁴⁴ and using the ionization thresholds reported in Figure 5, this contribution to the linewidth is estimated to be approximately 20 cm^{-1} . Besides the strong broad feature, some weak sharp features are observed at higher frequencies that do not vary with droplet size. The feature at the highest frequency, i.e., $23\,972 \pm 3\text{ cm}^{-1}$, can be assigned to the ionization of free excited $\text{Ba}(6s6p\ ^1P_1)$ atoms.⁴⁷ These atoms must have desorbed from the droplet after the excitation of the system since the excitation frequency of $18\,120\text{ cm}^{-1}$ is not resonant with the atomic transition. A careful analysis of the intensities reveals that the free barium signal corresponds to 1.6% of the total signal, indicating that indeed only a very small fraction of the excited barium atoms desorb from the droplets. The other peaks cannot be attributed to the barium atom and might correspond to small BaHe_n complexes.

3. Ion imaging

While the photoelectron and ZEKE spectra indicate that only a small fraction of the excited barium atoms desorbs from the droplets, the TOF mass spectrum seems to indicate that this fraction is significant. The apparent disagreement between these results might be accounted for by the dynamics associated with the ionization process. Whereas both photoelectron and ZEKE spectroscopy exclusively probe the properties of the neutral system, the TOF mass spectrum might to some extent reflect the dynamical processes following the ionization of the system. To test this hypothesis we have determined the velocity distributions of the ions by recording velocity map images. Figure 6 shows images for barium ions recorded at two different excitation frequencies within the absorption band. The images both show an isotropic distribution of similar size, indicating that the kinetic energy of the barium ions is independent of excitation frequency. This conclusion is confirmed by the speed distributions derived from the images. These observations are in strong contrast to what has been found for the excitation of alkali atoms on helium

FIG. 6. Ion images and corresponding kinetic energy distributions of barium ions detected following excitation of barium-doped helium droplets with a mean radius of 41 Å at two different frequencies within the $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ absorption band. The photon energy for ionization is $24\,155\text{ cm}^{-1}$. The two vertical lines indicate the energetic threshold for ions originating from desorbed $6s6p\ ^1P_1$ excited barium atoms.

droplets. Following excitation, the alkali atoms desorb from the droplets with well-defined and frequency dependent angular and speed distributions.^{12,15} The different behavior observed for barium suggests that the detected barium ions do not result from the ionization of desorbed atoms. This conclusion is corroborated by considering the energy balance of this process. Taking into account the binding energy of ground state barium to the helium droplets, the maximum energetically allowed kinetic energy of the desorbed barium atoms is $18\,148\text{ cm}^{-1}$ for excitation at $18\,120\text{ cm}^{-1}$ ($18\,250\text{ cm}^{-1}$). The kinetic energy distributions of the barium ions presented in Figure 6 extend well beyond these limits. Consequently, the ions cannot result from the ionization of desorbed atoms. We therefore attribute these ions to the ionization of excited barium atoms attached to the helium droplets.

Based on the energetics, one expects ions to be solvated by the helium.^{55,56} The mass spectrum presented in Figure 2 indeed indicates that some fraction of the ions remains attached to the droplets and thus possibly becomes solvated. However, as seen above, the photoionization of barium-doped helium droplets also yields bare barium ions with high kinetic energies. It is not clear by which process these ions are produced. Ejection of helium ions upon electron impact ionization of helium droplets was first reported by Gspann and was attributed to the localization of the solvation energy around the ion.⁵⁷ Later experiments on electron impact ionization of doped helium droplets have shown that helium atoms leaving the droplets can take away significantly more energy than their binding energy, which has been taken as an evidence of a non-thermal cooling mechanism.^{58,59} Recently, we have shown that vibrational excitation of molecular ions embedded in helium droplets is accompanied by a non-thermal cooling process which leads to the ejection of ions from the droplets with considerable kinetic energy.^{48,60} The presence of bare barium ions found in the present study appears to be another

manifestation of the non-thermal processes governing the solvation dynamics of ions. However, a clear picture of these processes is still lacking.

B. Ba(6s6d)

1. Excitation spectrum

Barium, being a two electron system, has an intricate electronic structure with many low lying excited states. For barium atoms attached to helium droplets the dipole selection rules of the free atom are relaxed due the reduced symmetry of the system. As a result, the complexity of the spectrum increases rapidly with excitation energy. Whereas the $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ transition discussed above is well isolated, this is not the case for states at higher energies. Due to the limited tuning range of the laser system excitation spectra could only be recorded for frequencies above $29\,600\text{ cm}^{-1}$, i.e., in the range where spectra start to overlap. The upper panel of Figure 7 shows the 1+1 excitation spectra of barium attached to helium droplets with a mean radius of 41 Å in the range of $29\,600$ to $32\,800\text{ cm}^{-1}$ recorded by monitoring the yield of Ba^+ , BaHe^+ , and BaHe_2^+ . Whereas the BaHe^+ and BaHe_2^+ excitation spectra are characterized by a single broad resonance extending from $30\,600$ – $32\,000\text{ cm}^{-1}$, the Ba^+ spectrum reveals a much more complex structure all the way down to

FIG. 7. Upper panel: Excitation spectra of barium-doped helium nanodroplets with a mean radius of 41 Å recorded by detecting Ba^+ , BaHe^+ , and BaHe_2^+ ions. The dashed vertical lines mark the energy of states in the free barium atom. Middle panel: Mean anisotropy parameter of barium atoms and BaHe_n complexes desorbed from the helium droplets after excitation. The horizontal lines correspond to the average anisotropy parameter for a given transition. Lower panel: Mean kinetic energy of the desorbed barium and BaHe_n complexes. The solid red line is a linear fit to the barium data. The dashed blue line is to guide the eye.

$29\,600\text{ cm}^{-1}$. Assignment of the spectral features is not straightforward due to the dense manifold of electronic states. Within the covered frequency interval, barium has two excited singlet states, $6s6d\ ^1D_2$ and $6s7p\ ^1P_1$, that are indicated by the dashed vertical lines in Figure 7. In addition, there are two singlet states at slightly lower energies, i.e., $5d6p\ ^1P_1$ and $6s7s\ ^1S_0$ at $28\,544$ and $28\,230\text{ cm}^{-1}$, respectively.⁴⁷ As the spectra of atoms on helium droplets for low principal quantum number are in general blue shifted compared to the free atom, these states are expected to contribute to the spectrum reported in Figure 7. The onset of the BaHe^+ and BaHe_2^+ excitation spectra occurs at a slightly higher energy than the $6s6d\ ^1D_2$ state. Hence, we tentatively assign these spectra to the $6s6d\ ^1D_2 \leftarrow 6s^2\ ^1S_0$ transition. In view of the similarity between these spectra and the spectral feature in the Ba^+ excitation spectra in the $30\,600$ – $32\,000\text{ cm}^{-1}$ interval we assign this feature to the same transition. Having assigned the high frequency part of the spectrum to the $6s6d\ ^1D_2 \leftarrow 6s^2\ ^1S_0$ transition, the low frequency part most likely involves the $6s7s\ ^1S_0$ or the $5d6p\ ^1P_1$ state.

2. Photoelectron spectra

Photoelectron spectroscopy can provide additional information on the character of excited states.¹² Since the helium environment does not induce significant relaxation for excited atoms with low principal quantum number, the character of the electronic state can be directly related to the internal energy of the desorbed atom. Figure 8 shows photoelectron spectra recorded at two different excitation frequencies within the absorption band. The spectrum recorded at an

FIG. 8. Photoelectron spectra of barium-doped helium nanodroplets with a mean radius of 41 Å recorded following excitation at two different excitation frequencies within the absorption band. The asterisk denotes ionization of states yielding excited $5d\ ^2D_{3/2}$ and $5d\ ^2D_{5/2}$ barium ions.

excitation energy of $32\,258\text{ cm}^{-1}$ is characterized by three strong features. Based on the energetics these features can all three be attributed to $\text{Ba}(6s6d\ ^1D_2)$ atoms. The peak at highest photoelectron energy results from the photoionization of $\text{Ba}(6s6d\ ^1D_2)$ yielding ground state $\text{Ba}(6s\ ^2S_{1/2})$ ions, while the two other peaks correspond to the formation of excited $5d\ ^2D_{3/2}$ and $5d\ ^2D_{5/2}$ barium ions. Hence, the photoelectron spectrum confirms the assignment of the high frequency part of the spectrum in Figure 7 to the $6s6d\ ^1D_2 \leftarrow 6s^2\ ^1S_0$ transition. The weak feature at a photoelectron energy of $\sim 8000\text{ cm}^{-1}$ can be assigned to $\text{Ba}(6s6p\ ^1P_1)$. The presence of $\text{Ba}(6s6p\ ^1P_1)$ might indicate that the helium environment induces relaxation of the excited barium. However, it is more likely that $6s6p\ ^1P_1$ state is populated by radiative decay of the excited $6s6d\ ^1D_2$ barium atoms, since the radiative lifetime of this state is comparable to the laser pulse duration.^{12,61}

The photoelectron spectrum recorded following excitation at $30\,912\text{ cm}^{-1}$, i.e., at the region where the low and high frequency part of the excitation spectrum overlap, is presented in the upper panel of Figure 8. This spectrum reveals two features in addition to those originating from $\text{Ba}(6s6d)$ that can be attributed to excited $\text{Ba}(5d6p\ ^1D_2)$ and $\text{Ba}(5d6p\ ^1P_1)$ atoms. The presence of $\text{Ba}(5d6p\ ^1P_1)$ strongly suggest that the low frequency part of the spectrum presented in Figure 7 corresponds to the $5d6d\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ transition. This conclusion is reinforced by the fact that the photoelectron spectrum gives no evidence of the presence of excited $\text{Ba}(6s7s\ ^1S_0)$. It is unlikely that $\text{Ba}(5d6p\ ^1D_2)$ results from a direct excitation to this state, as this would imply an extremely large shift of 8000 cm^{-1} for the excitation spectrum. It can be ruled out that $\text{Ba}(5d6p\ ^1D_2)$ results from radiative decay of $\text{Ba}(5d6p\ ^1P_1)$ since the transition probability is negligible.⁶² In view of the small energy difference between the $5d6p\ ^1D_2$ and $\text{Ba}(5d6p\ ^1P_1)$ states, $\Delta E \sim 5500\text{ cm}^{-1}$, and the fact that both states have the same electron configuration, it is most likely that efficient helium-induced relaxation of excited $\text{Ba}(5d6p\ ^1D_2)$ is responsible for populating the $5d6p\ ^1P_1$ state.

3. Ion Imaging

Following excitation the barium atoms desorb from the surface of the helium droplet. It has been shown before that the angular distribution of the desorbed atoms is directly related to the symmetry of the states involved.¹² At the same time, the kinetic energy distribution of the atoms carries information on the interaction of the excited valence electron with the helium droplet. Here, we have recorded velocity map images at several excitation frequencies within the excitation spectrum to confirm our assignment of the resonances. Selected images are presented in Figure 9. Inspection reveals a pronounced variation of both the angular and radial distributions with excitation frequency. These are strong indications that the excitation spectrum involves multiple excited states.

Quantitative information can be obtained by performing an inverse-Abel transformation on the images. The resulting kinetic energy distributions are presented in the lower panel of Figure 9. The anisotropy parameter β has been determined

FIG. 9. Upper panel: Velocity map images of barium ions recorded following excitation of barium-doped helium droplets with a mean radius of $41\text{ \AA}$ at different frequencies within the absorption band. The polarization of the light is vertical with respect to the images. Lower panel: Kinetic energy and anisotropy parameter distributions derived from the images shown above.

from the angular distribution, $I(\theta_{KE})$, using the relation

$$I(\theta_{KE}) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta_{KE})], \quad (1)$$

where θ_{KE} is the angle between the velocity vector of the atoms and the polarization of the light at a given kinetic energy and $P_2(\cos \theta)$ is the second Legendre polynomial.⁶³ The value of the anisotropy parameter β is directly related to the symmetry of the states involved. It takes the value of -1 for a perpendicular and $+2$ for a parallel transition.⁶³ The system having a $6s^2\ ^1S_0\ \Sigma$ ground state, a value of β close -1 ($+2$) denotes excitation to a Π (Σ) state.

Excitation at $29\,630\text{ cm}^{-1}$ yields a slightly asymmetric kinetic energy distribution that extends towards higher energies. The anisotropy parameter is found to vary strongly with the kinetic energy, yielding a value close to -1 for low kinetic energies and a value close to $+2$ at the highest energies. These observations indicate that two states of different symmetry contribute to the spectrum at this frequency. At the excitation frequency of $30\,303\text{ cm}^{-1}$ the kinetic energy

distribution is symmetric and the anisotropy parameter remains constant close to a value of +2, signifying that at this frequency a state of Σ symmetry is excited. In contrast, excitation at $30\,769\text{ cm}^{-1}$ yields two clearly resolved kinetic energy distributions. The angular distributions corresponding to the two kinetic energy distributions are noticeably different. The high kinetic energy distribution is characterized by an anisotropy parameter close to +2, suggesting that this distribution results from excitation to a Σ state. In contrast, the anisotropy parameter corresponding to the low kinetic energy distribution has a value close to zero. This suggests that these barium atoms result from excitation to a superposition of Σ and Π states. At higher excitation energies, the contribution of the high kinetic energy component decreases and eventually becomes zero, while the slow component moves towards higher kinetic energies.

To correlate the angular distributions with the excitation spectrum, the anisotropy parameters have been averaged over the kinetic energy distributions at each excitation frequency. The results are plotted in the middle panel of Figure 7. One clearly observes a strong correlation between the anisotropy parameters and the spectral features. In combination with the photoelectron spectra this allows us to assign the spectra. As the low frequency part of the excitation spectrum correlates to the $5d6p\ ^1P_2$ state of the free atom and is characterized by a mean anisotropy parameter of 1.49 ± 0.04 , indicative of a parallel transition, we assign this spectral feature to the $5d6p\ ^1P_1\ \Sigma \leftarrow 6s^2\ ^1S_0\ \Sigma$ transition. The high frequency part of the spectrum correlates to the $6s6d\ ^1D_2$ state of barium and is characterized by a mean anisotropy parameter of 0.33 ± 0.05 . Hence, we assign this feature to a superposition of the $6s6d\ ^1D_2\ \Sigma \leftarrow 6s^2\ ^1S_0\ \Sigma$ and $6s6d\ ^1D_2\ \Pi \leftarrow 6s^2\ ^1S_0\ \Sigma$ transitions. No photoelectron spectra have been recorded at around $29\,600\text{ cm}^{-1}$, and hence it is not possible to make a definite assignment of the sharp feature observed at this frequency. Based on the anisotropy parameter we conclude that the transition involves an excited state of Π symmetry.

The kinetic energy distributions of the desorbed atoms can provide additional information on the excited states.¹² The bottom panel of Figure 7 displays the mean kinetic energy of the distributions as a function of excitation energy. The mean kinetic energy of desorbed barium atoms resulting from excitation via the $6s6d\ ^1D_2\ \Sigma \leftarrow 6s^2\ ^1S_0$ transition depends linearly on the excitation frequency. This linear relation has been explained by an impulsive model,¹² according to which the mean kinetic energy of the desorbed barium atoms, $E_{kin}(\text{Ba})$, is given by

$$E_{kin}(\text{Ba}) = \frac{m_{eff}}{m_{eff} + m_{Ba}} [h\nu - E_{int}(\text{Ba}) - E_{bind}], \quad (2)$$

where $E_{int}(\text{Ba})$ is the internal energy of the desorbed barium, E_{bind} is the binding energy of the ground state barium atom to the helium droplet, and m_{eff} is the effective mass of the helium atoms interacting with the excited atom. By extrapolating the expression to zero kinetic energy, the internal energy of the desorbed barium atom can be determined. A linear fit to the data assigned to the $6s6d\ ^1D_2 \leftarrow 6s^2\ ^1S_0$ transition yields an internal energy of $30\,130 \pm 90\text{ cm}^{-1}$ for the desorbed barium atoms. This value is close to the energy of $6s6d\ ^1D_2$ state

of the free atom, and hence confirms the above assignment of this transition. In addition, the fit yields an effective mass of 17.3 amu for the helium. This value can be interpreted as that the excited $\text{Ba}(6s6d\ ^1D_2)$ atom interacts on average with 4.3 helium atoms. The number of interacting helium atoms is somewhat larger than that found for the corresponding $3d \leftarrow 3s$ transition of sodium.⁶⁴ This difference is thought to reflect the fact that barium is located in a more pronounced dimple on the surface of the helium droplets and therefore interacts with larger number of helium atoms. Finally, we would like to point out that the anisotropy parameters and mean kinetic energies for BaHe complexes reveal the same frequency dependence as the barium atoms, thereby confirming that Ba and BaHe spectra correspond to excitation of the same state.

The mean kinetic energy at lower excitation frequencies does not show a clear linear dependence on photon energy. This could indicate that the simple impulsive model used to describe the desorption process is not valid here. Alternatively, it might reflect that several excited states contribute to the excitation spectrum in this region or that the atoms undergo relaxation on a timescale comparable to that of the desorption of barium atoms from the droplets.

C. Rydberg states

1. Excitation spectra

For alkali-doped helium droplets it was found that the frequency shift and linewidth of the resonances increase initially with increasing principle quantum number n .^{11,13} For values of n where the mean electron orbit radius becomes larger than the droplet diameter, a redshift and narrowing of the resonances is observed.^{10,11} For the droplet sizes considered in this study, the transition is expected to occur for states of Ba with $n \sim 11$.^{65,66} Figure 10 shows a composite excitation spectrum in the region of $32\,000\text{--}42\,000\text{ cm}^{-1}$ recorded by monitoring the yield of Ba^+ ions. Indicated in the figure are selected singlet transitions of free barium. We would like to mention that no evidence of BaHe_n complex formation was observed in this spectral interval. Inspection of the spectrum reveals that the transitions in the low frequency range are significantly broadened and shifted towards higher energies with respect to the gas phase. For example, the $6s7p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ transition, which in the free atom is located at $32\,547\text{ cm}^{-1}$, is observed at about $34\,000\text{ cm}^{-1}$, corresponding to shift of $\sim 1500\text{ cm}^{-1}$ and has a width of $\sim 1000\text{ cm}^{-1}$. At an excitation frequency of about $39\,000\text{ cm}^{-1}$, corresponding to states with $n = 10\text{--}11$, the resonances in the spectrum suddenly become sharper, having a width of $\sim 100\text{ cm}^{-1}$ (FWHM). At the same time the transitions are shifted towards lower energies compared to the free atom. These transitions form part of the $6snp$ Rydberg series converging to Ba^+ (6s). Each member of the series consists of two partially overlapping transitions. This reflects the energy difference of states having different projections of the angular momentum onto the symmetry axis of the system, i.e., $\Lambda = 0$ and $\Lambda = 1$, caused by helium-induced configuration mixing.¹⁰ Unfortunately, the transitions quickly merge into a continuum which hampers a detailed analysis of the Rydberg series. From the spectrum, which has been

FIG. 10. Upper panel: Excitation spectrum of barium-doped helium nanodroplets with a mean radius of 41 Å recorded by monitoring the yield of barium ions. Indicated on the top are the energy levels of selected singlet states of the barium atom. Middle panel: Mean anisotropy parameter of barium atoms desorbed from the helium droplets after excitation. The dashed vertical lines show the correlation between spectral features in the excitation spectrum and the mean anisotropy parameter. Lower panel: Mean kinetic energy of the desorbed barium atoms.

recorded under field free conditions, it is clear that the ionization threshold for Ba attached to helium droplets is lower in energy than that of free barium. Spectra recorded using different droplet sizes reveal that the threshold shifts toward lower energies for larger droplets. These observations are in agreement with the results from the photoelectron and ZEKE spectra recorded via the 6s6p state of barium, described above.

2. Ion imaging

It is expected that the change in interaction of the barium with the helium with principal quantum number is also reflected in the kinetic energy distributions of the desorbed barium atoms. Therefore ion images have been recorded at selected excitation frequencies. While the kinetic distributions up to an excitation frequency of 36 000 cm⁻¹ are mostly composed of multiple contributions, at higher frequencies they are all characterized by a single, almost Gaussian distribution. The mean average kinetic energy and anisotropy parameter of the desorbed barium atoms calculated from the distributions are plotted as function of excitation frequency in the lower panel of Figure 10.

As before, the anisotropy parameter can be used to characterize the symmetry of the excited state. For example, the anisotropy parameter changes from a negative to a positive value within the broad absorption band around 34 000 cm⁻¹

that has been assigned to the 6s7p ¹P₁ ← 6s²1S₀ transition. This signifies that the low frequency part of this spectral feature is related to the corresponding Π ← Σ transition while the high frequency part corresponds to the Σ ← Σ transition. This nicely confirms the general trend that Σ states are higher in energy than Π states due to the stronger repulsion between the excited atom and the helium.¹¹ At frequencies around 39 000 cm⁻¹ a strong variation of the anisotropy parameter with excitation frequency is observed. Closer inspection reveals that negative values correspond to the high frequency components of the 6snp Rydberg members, while positive values correlate to the low frequency components. This allows us to identify the higher and lower energy states as 6snp Π and 6snp Σ, respectively.

At low excitation frequencies, the average kinetic energy of the desorbed barium atoms does not reveal a systematic variation with photon energy. This might be expected since in this region states of different character contribute to the spectrum. In contrast, at frequencies above 37 000 cm⁻¹ the mean kinetic first systematically increases with excitation energy before it starts decreasing again at 39 000 cm⁻¹. As discussed above, at this frequency the excitation spectrum changes character due to the fact that the electron orbit radius becomes comparable to the droplet size. The resulting change in interaction between the Ba and the helium droplet thus appears to be directly reflected in the mean kinetic energy of the desorbed Ba atoms. These results on barium are in line with experiments on sodium-doped helium droplets where it was found that the decreasing interaction strength was accompanied by a longer residence time of the excited atoms on the surface of the helium droplets.¹⁰

D. Photoionization

1. Photoelectron and ZEKE spectra

The ionization threshold for barium atoms on helium droplets cannot be determined by extrapolation of the Rydberg series, as only a few isolated transitions could be identified in the excitation spectrum. However, an accurate determination is possible using other spectroscopic techniques. In a first step we have tried to determine the ionization threshold from photoionization spectra recorded by monitoring the yield of ion-containing helium droplets. The bottom panel of Figure 11 shows the photoionization spectrum for barium attached to helium droplets with a mean radius of 41 Å. The spectrum is characterized by a pronounced onset of the ion yield at about 41 800 cm⁻¹. The ion yield initially increases with excitation frequency before leveling off at approximately 42 200 cm⁻¹. Closer inspection of the spectrum reveals a slight change of slope of the ion yield at a frequency of about 41 900 cm⁻¹. In combination with the limited signal-to-noise ratio, this hampers a reliable determination of the ionization threshold. However, it is clear that the threshold is noticeably lower than that of the free atom, which is located at 42 035 cm⁻¹.⁴⁷

Additional information on the ionization threshold can be obtained by photoelectron spectroscopy. Unfortunately, the large amount of electrons created by scattered UV light

FIG. 11. Upper panel: Photoelectron spectra of gas phase Ba and Ba attached to helium droplets with a mean radius of 41 Å recorded following two-photon ionization at 21 141 cm^{-1} . Middle panel: ZEKE spectrum of barium-doped helium nanodroplets recorded using one-photon excitation. The theoretical spectrum for BaHe_{3000} based on the pseudo-diatomic model is shown for comparison. The droplet size dependence of the ZEKE spectrum is presented in the insert. Lower panel: Photoionization spectrum recorded by detecting BaHe_n^+ , $n > 30$, complexes. The integrated ZEKE signal, corrected for the Ba background signal, is also shown. The vertical dotted line corresponds to the inflection point in the photoionization spectrum and the onset of the tail in the ZEKE and photoelectron spectrum.

makes it practically impossible to record photoelectron spectra using direct one-photon ionization. Therefore spectra have been recorded by non-resonant two-photon excitation using a frequency of 21 141 cm^{-1} . This frequency is well outside the absorption band of the $6s6p\ ^1P_1 \leftarrow 6s^2\ ^1S_0$ transition and to the red of any other atomic transition in barium, thereby ensuring non-resonant ionization of the system. The resulting photoelectron spectrum presented in the upper panel of Figure 11 is characterized by a single broad peak. Similar spectra have been recorded for other droplet sizes. For an accurate determination of the ionization threshold, the photoelectron spectrum of free barium has been recorded under identical experimental conditions, see Figure 11. Analysis of the spectra reveals that the ionization threshold is lowered by approximately 200 cm^{-1} , depending on droplet size, see Figure 5. The droplet size dependence is similar to that observed in the photoelectron spectra recorded via excitation of the $6s6p\ ^1P_1$ state of barium, except for the magnitude of the shift. Whereas ionization via the $6s6p\ ^1P_1$ state indicates a lowering

of the ionization threshold of approximately 100 cm^{-1} , direct ionization yields a shift of about 200 cm^{-1} .

Closer inspection of the photoelectron spectrum presented in Figure 11 reveals that the peak is slightly asymmetric towards lower kinetic energies. Although free barium contributes to the signal in this region of the spectrum, it cannot fully account for the observed lineshape. More detailed information on the lineshape can be obtained from high resolution ZEKE spectra. The ZEKE spectrum recorded via one-photon excitation is shown in the middle panel of Figure 11. The spectrum is characterized by peak followed by a tail that extends several 100 cm^{-1} towards higher frequencies on top of which a narrow (4 cm^{-1} FWHM) symmetric feature is located. The sharp feature is readily identified as the ZEKE spectrum of free barium, while the broad structure can be assigned to barium attached to helium droplets. The shape of this resonance is compatible with the asymmetric lineshape observed in the photoelectron spectrum, although it should be noted that the tail is more pronounced in the ZEKE spectrum. Spectra recorded at different droplet sizes, see inset middle panel Figure 11, reveal that the onset of the ZEKE spectrum shifts towards lower frequencies and that the intensity of the high frequency tail increases with increasing droplet size. The shift of the ZEKE spectrum has been analyzed by fitting the low frequency part of spectral feature to a Gaussian line profile. Figure 5 shows the shift as function of droplet size. The results compare reasonably well to the shifts determined by photoelectron spectroscopy.

2. Discussion

The lowering of the ionization threshold of the BaHe_N system with respect to the free atom is found to depend on the excitation pathway. Whereas direct ionization indicates a lowering of the ionization threshold of approximately 200 cm^{-1} , ionization via the $6s6p\ ^1P_1$ state yields a shift of about 100 cm^{-1} . This difference can be rationalized by considering the interaction potentials of the barium atom and ion with the helium droplet. The interaction potentials for neutral barium, which have been discussed in detail above, are displayed in Figure 3 together with interaction potential for the ion. This latter has been determined within the pseudo-diatomic model using the ground state Ba^+-He pair potential.^{67,68} The ionization threshold has been determined by simulating the ZEKE spectrum as the Franck-Condon factors for vibronic transitions from the ground state of the neutral to that of the ion.¹⁰ The Franck-Condon factors have been calculated from the effective interaction potential shown in Figure 3 using the LEVEL 8.0 program.⁶⁹ The theoretical spectrum which is depicted in the middle panel of Figure 11 is characterized by a Gaussian distribution that is shifted towards lower energy with respect to the free atom. As in the case of sodium,¹⁰ the calculations slightly underestimate the observed lowering of the ionization threshold but reproduce the droplet size dependence fairly well, see Figure 5.

The experiments reveal that following excitation of $6s6p\ ^1P_1$, the system relaxes to a stable configuration before being ionized by the absorption of a second photon. Since the potential energy curves shown in Figure 3 have been

calculated within the Franck-Condon approximation which does not take into account the rearrangement of the helium after excitation, these potential energy curves cannot be used to calculate the ionization threshold. A determination of the ionization threshold requires effective interaction potentials for the excited $6s6p\ ^1P_1$ state of the neutral and the ground state of the ion that are based on the helium density optimized for the $6s6p\ ^1P_1$ state. Unfortunately, no such helium density profiles are available. One can therefore only speculate to what extent the potentials will be modified by the rearrangement of the helium. From experiment it is, however, clear that the overall effect results in a smaller reduction of the ionization threshold.

The lineshape of the ZEKE spectra reported in Figure 11 differ significantly from that of the spectra recorded via the $6s6p\ ^1P_1$ state, see Figure 4, or those of Na and Ag atoms attached to helium droplets.^{10,43} Those ZEKE spectra are all characterized by a Gaussian lineshape, which is thought to reflect the radial delocalization of the impurity atom on the helium droplets. To determine whether the peculiar lineshape observed for barium in the present study is due to the delocalization of the ground state barium atom, we compare the spectrum to the simulated ZEKE spectrum shown in the middle panel of Figure 11. Since the theoretical spectrum is characterized by a Gaussian distribution, this strongly suggests that the high frequency tail observed experimentally is not related to the radial delocalization of the barium atom on the surface of the droplets. The possibility that the high frequency tail is related to the angular delocalization of the barium, which is not considered here, can be ruled out, as it cannot account for the presence of the ZEKE signal more than 500 cm^{-1} above the ionization threshold of the free atom. Hence, another mechanism has to be responsible for the characteristic lineshape.

Barium, being a two electron system, has a rather complex energy level structure which is characterized by Rydberg series converging to the $6s\ ^2S_{1/2}$ ground state and the excited $5d\ ^2D_{3/2}$ and $5d\ ^2D_{5/2}$ states of the barium ion. Rydberg states above the first ionization threshold converging to an excited ionic state autoionize due to configuration interaction and give rise to Beutler-Fano profiles in the photoionization spectrum. In the energy region close to the ionization threshold two autoionizing Rydberg states, $5d8p\ ^1P_1$ and $5d5f\ ^3P_1$, have been identified.⁷⁰ One expects that the interaction giving rise to the structure in the photoionization spectrum will be affected by the presence of helium since the ionization threshold is lowered by the helium while Rydberg states having low principal quantum numbers are shifted up in energy. However, it is unclear how exactly this will modify the photoionization spectrum. It might thus well be that the observed change in slope in the photoionization spectrum shown in the bottom panel of Figure 11 is related to the presence of an autoionizing state, even though there is no counterpart in the free atom at this frequency. In light of this, it is important to note that the change in slope occurs at the same frequency at which the tail in the ZEKE spectrum starts. To highlight the relation between the ZEKE and the photoionization spectrum we have plotted the integrated ZEKE spectrum in the lower panel of Figure 11. Indeed, the integrated ZEKE spectrum shows

a similar change of slope as observed in the photoionization spectrum. Normally, structure in the photoionization spectrum does not manifest itself in ZEKE spectra. However, it has been found that ZEKE spectra can be strongly affected by dynamical processes following the excitation of high Rydberg states.⁷¹ In this case, the tail in the ZEKE spectrum could possibly be a signature of the presence of an autoionizing state. The fact that this structure is not observed in the ZEKE spectra recorded via the $6s6p\ ^1P_1$ state does not refute this possibility as the structure in the photoionization, and thus possibly ZEKE spectrum depends on the excitation path. Clearly, more experimental and theoretical work is required to test this hypothesis.

IV. CONCLUSION

Excitation spectra of barium atoms located on the surface of helium nanodroplets have been recorded. Even though barium atoms are located in a deeper dimple than alkali atoms, their excitation spectra share the same characteristics. The transitions involving states with low principal quantum number are characterized by broad resonances that are significantly shifted towards higher energies compared to the corresponding gas phase transitions. The broadening and shift of the resonances can be attributed to the repulsive interaction of the excited valence electron with the helium. Spectra involving high Rydberg states reveal significantly narrower resonances which are shifted towards lower energies compared to the free atom. The narrowing of the lines reflects the reduced repulsive interaction of the electron with the helium when excited to an orbital with a mean radius that is comparable to or larger than the size of the helium droplet. Photoionization, photoelectron, and ZEKE spectroscopy indicate that the redshift of the spectra is caused by a lowering of the ionization threshold due to polarization of the helium by the barium ionic core. The lowering of the ionization threshold is found to depend on the internal energy of the barium atom. This has been attributed to a difference in solvation energy of barium atoms in different electronic states and the dependence of the ionization threshold on the distance between the atom and the droplet.

Following excitation, the barium atoms desorb from the surface of the helium droplets due to the overall repulsive interaction of the excited atom with the helium. Only when excited to the $6s6p\ ^1P_1$ state, which reveals an attractive interaction with the helium, the atoms remain attached to the droplets. The speed and angular distributions of the desorbed atoms are found to be state specific and can be used for the assignment of the excitation spectra. While the angular distribution provides information on the symmetry of the excited state, the frequency dependence of the mean kinetic energy yields the energy of the correlating atomic state and the average number of helium atoms interacting with the excited barium atom. In the case of $6s6d\ ^1D_2$ excited barium, the mean number of interacting helium atoms is found to be 4.3, which is somewhat larger than that for the corresponding state of Na. This difference has been attributed to the location of the barium atom in a more pronounced dimple structure. For the higher Rydberg states, the speed distributions of the

desorbed atoms show a systematic dependence on the principal quantum number, reflecting the change in interaction of the excited atom with the helium as the orbital radius of the electron increases.

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