Formation of K^*He Exciplexes on the Surface of Helium Nanodroplets Studied in Real Time

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Superfluid helium nanodroplets are doped with potassium atoms to form complexes with the alkali atom residing on the surface of the droplets. Dispersed laser-induced fluorescence spectra of such systems already revealed the formation of M^*He (M = Na, K) exciplexes upon electronic excitation [Reho *et al.*, Faraday Discuss. **108**, 161 (1997)]. By means of femtosecond pump-probe spectroscopy, this formation process now is followed in real time. We find $K^*He_{n=1}$ to be formed within 180 fs. Furthermore, the existence of exciplexes with $n > 1$ is quantified suggesting that the first ring around the potassium atom contains four helium atoms.

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Helium nanodroplet isolation (HENDI) has been established as a useful tool for spectroscopically interrogating molecules and weakly bound complexes at very low temperatures [1,2] and for probing the size dependence of the properties of superfluid helium [3,4]. Since the first infrared spectra of helium droplets doped with SF_6 obtained by Scoles and co-workers in 1992 [5], a variety of spectroscopic tools have been introduced to probe guest species in this ultracold ($T \approx 380$ mK) environment: electronic excitation spectroscopy (using either laser-induced fluorescence [6,7] or beam depletion [3,8,9] detection), Stark spectroscopy [10], microwave single and double resonance [11], microwave-infrared double resonance [12,13], photodetachment [14], and photoionization spectroscopy [15,16]. Furthermore, the formation of unusual weakly bound complexes and new conformers appears to be an interesting new direction in this field [17–20].

Although there is no question about the applicability of HENDI for high resolution spectroscopy at very low temperatures, our basic understanding of these quantum systems is still incomplete. For instance, the momentum transfer during the pickup of molecules, the possible existence of vortices, and the helium response to the optical excitation of atoms and molecules are all in need of further study. In particular, the dynamics of these systems appears to be a fascinating issue because of their superfluid property. Much progress has been made from the theoretical point of view in understanding the dynamics of molecular rotation in helium droplets [21,22] explaining the reduction of rotational constants that molecules display in the environment of the droplet. From spectroscopic experiments of embedded laser-excited molecules, vibrational and rotational relaxation times have been estimated [23,24]. An alternative way to study dynamics is via time resolved experiments, which have been proven to be a valuable tool to probe the time evolution of many molecular systems directly [25].

Recently, we have shown the applicability of femtosecond pump-probe spectroscopy for the study of doped helium droplets [15]. Potassium atoms on the surface of helium nanodroplets were chosen as the first target because this system is well characterized through absorption and emission spectra of its $p \leftarrow s$ electronic transition [26]. In addition, time-dependent studies have been carried out by means of time correlated single photon counting using picosecond lasers [27,28]. A peculiarity in the excitation of light alkali atoms on the surface of the helium droplet is the formation of alkali-helium exciplexes which form when one or more He atoms are attracted into the nodal plane of the excited p orbital. Real-time studies of such a formation process give basic information on the interaction of the constituents and the structure of the product molecules; applications to chemical reaction or transition state studies at very low temperatures are evident.

In bulk liquid helium, fluorescence of laser-excited light alkalis was not found. The formation of M^*He_n ($n \approx 5$) exciplexes have been proposed as the cause of the quenching of fluorescence emission. In these exciplexes the crossing between the excited and the ground state potential energy surface opens the possibility of a decay via nonradiative transitions [29–31]. This does not apply to the heavier alkalis (Rb, Cs), where the curve crossing mentioned above is not present due to the larger atomic cores and the stronger spin orbit coupling. In this case, the He atoms are not allowed to approach the waist of the p orbital as much as in the case of Li and Na. In contrast to bulk helium, fluorescence spectra of light alkalis (Li, Na, K) attached to helium droplets have been recorded upon $p \leftarrow s$ excitation [26]. Moreover, from analysis of the emission spectra and from time-correlated measurements, the following conclusions have been derived [27,28,32]: Emission takes place after desorption from the droplet's surface only. Alignment of the excited state, i.e., selection of Σ and Π symmetry, can be achieved by variation of the excitation frequency: The enhanced repulsion in the

Σ geometry shifts the absorption to the blue of the Π absorption spectrum. Exciplexes are not formed when the p orbital is aligned perpendicularly to the helium surface (Σ excitation); in this case the bare atom desorbs. Aligning the p orbital parallel, mainly the M^*He (M = Na, K) diatomic exciplex forms. Desorption appears to reduce the probability to collect more helium atoms. Both processes, direct desorption of the potassium atoms and formation of K*He take place with time constants around 50 ps. Along the $^2\Pi_{1/2}$ path, an even much slower component (7.9 ns) in the formation of the exciplex was found [28].

In this Letter we report the first direct experimental observation of the formation of K*He exciplexes on the surface of a helium nanodroplet. The experimental setup used in the study is similar to the one used in the earlier experiments [15]. Helium gas is expanded at high stagnation pressure (5×10^6 Pa) and low temperature (19 K) through a 10 μm orifice into vacuum to produce a beam of clusters which contain 5000 helium atoms on average. The droplets are doped with single potassium atoms by collisions inside an oven containing an appropriate alkali vapor pressure. Further downstream, two collinearly propagating femtosecond light pulses, (FWHM $\approx$ 100 fs) from a titanium:sapphire laser, intersect the beam perpendicularly to photoexcite and ionize the doped droplets. The ions produced can either be collected by a microchannel plate, or mass selected in a quadrupole analyzer with a secondary electron multiplier detector. The pump-probe setup comprises a standard Michelson arrangement with a commercial translational stage for changing the delay times. The pump pulse prepares the chromophore in the first electronic excited state ($4p \leftarrow 4s$), whereas the probe pulse produces ionization in a two-photon step with roughly 0.5 eV excess energy. The improvements in the setup with respect to the experiments already published [15] are the mass selection of the ions and a decrease in the minimal step size to set the delay time between the pump and the probe pulse which leads to the enhanced resolution of 0.25 fs.

The results from the mass selected ion detection directly confirms the exciplex formation exclusively through the Π-excitation mechanism. In Fig. 1 two mass spectra are plotted: In the upper one the excitation laser was set to a frequency selecting preferentially Σ excitation at 12 990 cm^{-1}. In this case only bare potassium ions are detected. The lower panel, where Π alignment at 12 900 cm^{-1} is selected, clearly reveals the formation of potassium helium exciplexes. One cannot establish only that the main product is the K*He as has already been observed from the cw-spectroscopic data, but one can also quantify the abundance of the higher order exciplexes. To do this, one has to assume (i) equal ionization probabilities for the different species and to neglect (ii) fragmentation during ionization and detection. Hypothesis (i) is likely to hold because the attached helium atoms cause only minor perturbations in the potassium electronic structure. In the case of fragmentation, e.g., KHe$^+$ $\rightarrow$ K$^+$ + He the time-dependent structure of the exciplex has to appear on the K$^+$ mass channel also. We observe no residual structure from the KHe spectrum when selecting K; this supports (ii), at least for this fragmentation channel.

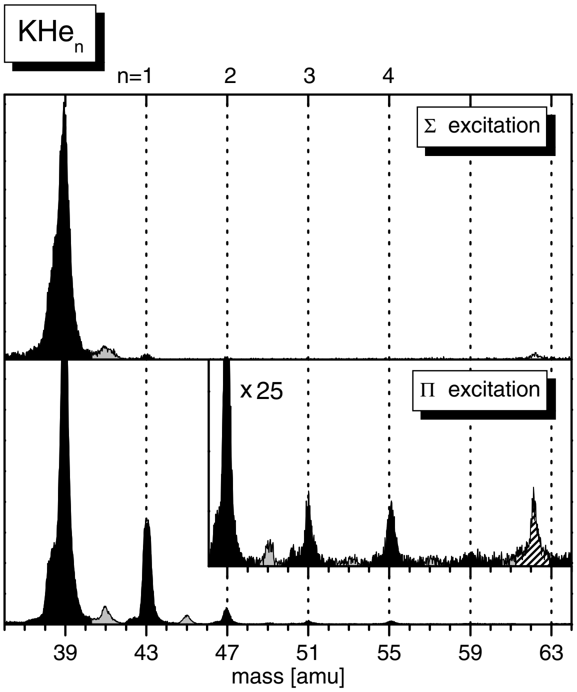

FIG. 1. Mass spectrum from photoionization of potassium-doped helium nanodroplets with a pair of femtosecond laser pulses separated by 100 ps. The spectrum in the upper panel is recorded at a photon energy of 12 990 cm^{-1}; in the lower panel, exciting at 12 900 cm^{-1}, exciplex formation is observed. The peak at mass 62 is due to KNa molecules. The peaks shaded in gray correspond to ^{41}K and its exciplexes.

The integrated peak intensities from Fig. 1 are displayed in Fig. 2. The estimate of 10% made in Ref. [32] of the number of K*He$_2$ molecules formed under the same excitation conditions fits well with the yield shown in Fig. 2.

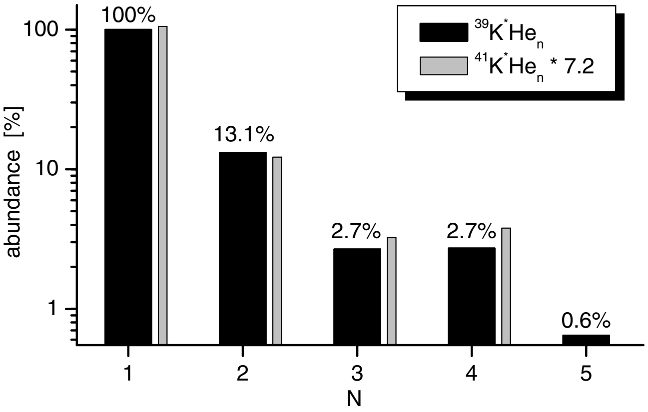

FIG. 2. Yield of higher order exciplexes by integration of the measured peaks. The bars in gray represent the intensity of the isotopomers containing ^{41}K multiplied by a normalizing factor obtained from the natural isotopic abundance.

Interesting to note is the sharp drop after the attachment of the fourth helium atom. We interpret this as a consequence of filling the first ring of atoms in the nodal plane around the *p* orbital; the attraction for additional atoms to form a second shell appears to be much weaker. From the almost equal abundances of the $n = 3$ and $n = 4$ exciplexes, one cannot conclude equal formation rates. Higher order exciplex formation as the main decay channel is missing to diminish the $n = 4$ intensity. The number of atoms in the first ring has been calculated for the $\mathrm{Na^*He}_n$ exciplex: Kanorsky *et al.* obtain five helium atoms [29], Dupont-Roc estimates five to six [30], and DeToffol *et al.* find four atoms in the first shell from density functional calculations [33].

In our femtosecond pump-probe setup, the formation process can now be analyzed in real time. In Fig. 3, time spectra are plotted setting the laser frequency to 12 900 cm^{-1} and detection on mass 39 (K^+) and mass 43 (KHe^+), respectively. Plotted are the signals normalized to the laser intensity. The curves are smoothed so that the superimposed rapid oscillation at the optical frequency is smeared out. These oscillations with a period of 2.6 fs are nicely resolved in the original data and are due to quantum interferences, originating from the phase correlation of the pump and probe pulses [15,34]. They will be presented in a separate publication [35] because introducing and interpreting the feature is beyond the scope of this Letter. A comparison of the K and the KHe intensities (Fig. 3) clearly shows a decrease of the KHe yield towards zero delay time between the pump and the probe laser pulse, confirming the absence of exciplexes at $t = 0$. The characteristic time of formation in this measurement is very short. We observe the maximum of intensity already after 250 fs. This explains some remaining intensity of KHe^+ at the origin because even within the width of the 100 fs laser pulse the excited complexes can be probed. For a first examination of the formation of the $\mathrm{K^*He}$, a fit is included in Fig. 3. A model for the intensity is chosen as a product of an exponential increase and an exponential decay where the decay converges to a finite value $h_0 > 0$:

$$I(t) = N[1 - \exp(-t/\tau_1)][\exp(-t/\tau_2) + h_0].$$

In this representation, τ_1 gives the formation time of KHe, and τ_2 is the characteristic time for a decrease in the detection of KHe. h_0 is a measure for the terminal KHe formation probability, and N is used for normalization. Assuming that the detection probability of desorbed exciplexes does not differ much from that of the exciplexes still on the surface, τ_2 directly represents the formation of KHe_2 [36]. We obtain $\tau_1 = 180 \pm 60$ fs, $\tau_2 = 204 \pm 60$ fs. Note that τ_1 and τ_2 are constrained to comparable times which is reasonable presuming the attraction of the second helium atom is not much weakened by picking up the first one. The production of higher exciplexes is the only decay channel for the detection of KHe. For a thorough exploration of all the formation times ($\mathrm{K^*He}_n@\mathrm{He}_N \rightarrow \mathrm{K^*He}_{n+1}@\mathrm{He}_{N-1}$, $n = 0, 1, \ldots$) and also desorption times ($\mathrm{K^*He}_n@\mathrm{He}_N \rightarrow \mathrm{KHe}_n + \mathrm{He}_N$) of all species, one has to measure the time spectra of all products and solve the coupled rate equations. This will be the object of future experiments.

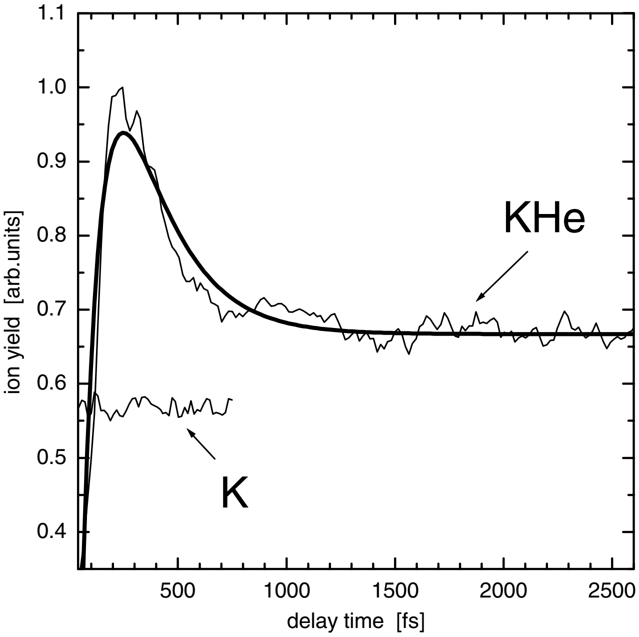

FIG. 3. Ion intensity as a function of delay time between two laser pulses recorded on mass 39 and mass 43 representing K and KHe, respectively. Smoothed ion intensities are shown to suppress an underlying quantum interference structure. The KHe intensity is compared to a fit with the function given in the text including an exponential growth and decay with $\tau_1 = 180 \pm 60$ fs and $\tau_2 = 204 \pm 60$ fs, respectively.

Our result points to much shorter formation times of the KHe exciplex compared to the value of 50 ± 20 ps ($^2\Pi_{3/2}$ excitation) and 7.9 ns ($^2\Pi_{1/2}$ excitation), respectively, from the earlier experiment by Reho *et al.* [27,28]. An assignment to a specific spin-orbit component cannot be attained from our data. The result also sets an upper bound to the desorption time after electronic excitation in the Π configuration. In order to prevent all the atoms forming higher order exciplexes the desorption has to take place within a time interval of less than 1 ps. This fast desorption could be originated in the relaxation of the vibrational energy involved in the formation of the exciplex. Even the first vibrationally excited state of the $\mathrm{K^*He}$ molecule comprises 75 cm^{-1} energy [32] already much above the binding energy to the surface of the cluster, which is in the range of 15 cm^{-1}.

One might argue that the helium atoms are picked up by the ion and that time spectra do not represent the formation of exciplexes in the first excited state. Although one could propose a "late" pickup, still the measured pump-probe signal can only mirror a dynamics in the intermediate state. The origin could in principle be any rearrangement. We believe the time spectra show the exciplex formation in the excited state because (a) at delay time $t = 0$ there is the most pronounced difference in the ion yield in Fig. 3 [37]. This discards a rearrangement of atoms because the nuclear motion is expected not to be much faster than the laser pulse duration. (b) The strongly attracted first shell of helium atoms by K^+ has an octahedral structure; so there should be no cutoff after having four atoms attached. (c) We do not see any attached helium in the case of the Σ excitation [38] and also probing Cs or K_n, $n \geq 1$. (d) The frequency of the rapid oscillations confirms the origin of pumping a one photon transition for that process. (e) The LIF experiments confirm the exciplex formation without any ionization.

In conclusion, we measured the relative abundance of exciplexes formed upon electronic excitation of potassium atoms on the surface of helium nanodroplets by means of photoionization and mass selection in a femtosecond pump and probe setup. We confirm that the K^*He exciplex remains as a most prominent product due to a rapid desorption from the cluster's surface. The measured intensities of the less abundant higher exciplexes suggest a closure of the first ring around the excited p orbital after the fourth helium atom has been captured. Time dependence of the ionized species signal gives information on the exciplex formation and desorption dynamics. The characteristic formation time for K^*He_n $(n = 1, 2)$ is determined to be on the order of 180 fs.

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[36] It is safe to assume that the formation of higher exciplexes is a sequential process and, as seen from the abundances in Fig. 2, also a minor channel.

[37] The ionic K^+ is spherically symmetric and does not remember any orientational effects.

[38] The shift in frequency of only 100 cm^{-1} is negligible compared to the ionization access energy of 4000 cm^{-1}.