Coherence and Relaxation in Potassium-Doped Helium Droplets Studied by Femtosecond Pump-Probe Spectroscopy

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Superfluid helium droplets are doped with potassium atoms to form complexes in which the metal atom is weakly bound to the cluster surface. The dynamics of these systems upon electronic excitation of the metal atom is probed by means of femtosecond pump-probe spectroscopy. Alignment of the excited potassium p orbital parallel to the cluster surface leads to quantum interferences, the decay of which gives information on the ultrafast perturbation of the induced atomic coherence by the superfluid environment; exciting the p state aligned perpendicularly, the strong repulsive interaction with the helium surface comes into play and the response of the helium environment is followed in time.

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Spectroscopic studies of doped helium clusters have developed into a strongly expanding field during the past two years [1,2]. Their unique properties make these cold ($T = 370$ mK [3]) droplets an ideal tool for investigations in quite different areas: they permit one to study the superfluid property of helium [4]; they can be employed as an ultracold and weakly perturbing matrix for high resolution molecular spectroscopy [1]; they allow one to form weakly bound complexes such as, e.g., high-spin states of alkali molecules [5]; bubble formation in the superfluid helium environment can be investigated by attaching metal atoms [6–8]. Also dynamic effects have been studied by Reho *et al.* [9] using picosecond lasers on alkali-doped large helium clusters, covering a time domain of several tens to hundreds of picoseconds.

With the availability of lasers generating pulses in the sub-100 fs regime, real-time spectroscopy has become feasible to probe the dynamics of such systems down to fs time scales. This is the topic of this Letter. In the brief history of femtosecond lasers many molecules and clusters have been studied following the pioneering work of Zewail and co-workers [10,11]. Owing to their relatively easy experimental as well as theoretical handling, alkali systems act as excellent prototypes (see [12] and references therein). A variety of ultrafast phenomena such as wave packet propagation [13], intramolecular vibrational redistribution (IVR) [14], and photodissociation have been observed. Coherent phenomena were first seen in cesium dimers [15] and, very recently, quantum coherence was detected in potassium and cesium atoms [16]. In this paper, we use the coherently excited potassium atom to probe the ultrafast dynamics in a K-He$_N$ system ($N \approx 5000$) or, from an atomic physics point of view, we want to know how fast the helium cluster will perturb the atomic excited state coherence. Hence, this experiment establishes a link between atomic and condensed matter physics, thereby providing a novel and efficient tool for probing the coherence and excited state wave packet dynamics of such complex systems.

The setup for generating a metal-doped helium cluster beam is similar to the one described earlier for cw spectroscopy [8,17]. The clusters condense in a supersonic expansion of helium gas from a cold nozzle at high stagnation pressure. After passing through a skimmer, they pick up single K atoms in a heated oven containing potassium metal; the energy involved in the atom-cluster collision process is dissipated by evaporative cooling of the helium cluster which rapidly returns to its temperature of 370 mK [3]. From previous work [6,18] it is known that alkali atoms reside in a shallow dimple on the clusters' surface [19]. In a separate vacuum chamber located farther downstream, the doped cluster beam intersects at right angles with the ultrashort pulses from a mode-locked titanium-sapphire laser which is tuned to the $4p \leftarrow 4s$ electronic transition of the K chromophore. A pulse duration of 90 fs (FWHM) has been estimated from interferometric autocorrelation traces. The Fourier-limited spectral width of these pulses is approximately 175 cm^{-1} (FWHM), sufficient to coherently excite the atomic K $4p_{1/2,3/2}$ states. A Michelson-type arrangement is used to produce pairs of collinearly propagating laser pulses with an adjustable time delay between the first (pump) and the second (probe) pulse. Ions resulting from three-photon ionization of the K atoms are detected in a channeltron detector.

In our first step, we probed free potassium atoms which evaporated effusively from the pickup oven after its temperature had been raised to values much higher than necessary for single-atom capture by the clusters [Fig. 1(a)]. Near zero delay (grey shaded area) the strong optical interference signal from direct overlap of the pump and the probe pulse appears in the ion intensity (autocorrelation peak at the optical period of 2.56 fs).

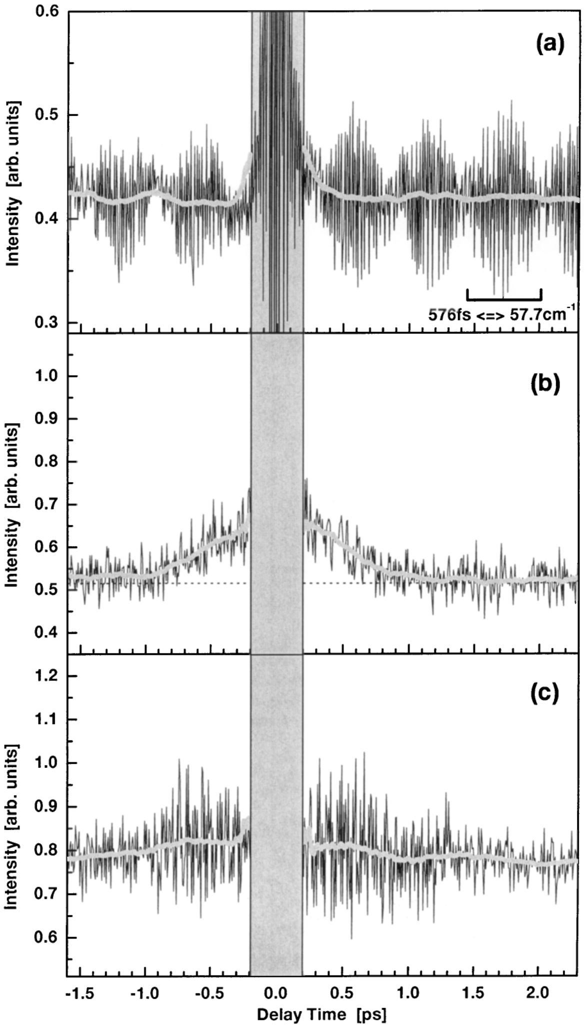

FIG. 1. (a) Ion intensity from three-photon ionization of gas-phase potassium atoms in a pump-probe experiment as a function of delay time, obtained by exciting the effusive beam from the pickup cell. The thick grey line gives the averaged intensity. (b) Same as above but exciting potassium-doped helium clusters at a frequency of 13 190 cm^{-1} (Σ excitation). In (c) the laser is tuned to 12 984 cm^{-1} (Π excitation). The broad grey bar covers the autocorrelation of pump and probe photons.

Outside that region we see the quantum interference structure known from earlier studies in which also the theory of this effect has been worked out in detail [16]: two quantum pathways which lead via the $4p$ state of potassium to the final ion state, separated in time by the delay between the pump and the probe pulse, generate the observed rapid interferences. Because of the fine structure splitting of the intermediate state ($4p_{1/2} - 4p_{3/2}$, $\Delta E = 55.72$ cm^{-1}), this rapid interference pattern displays a superimposed amplitude modulation with a period of 576 fs. In our experiment we were able to follow this pattern to very long pump-probe delays exceeding 100 ps. When probing the doped clusters, however, a quite different time structure of the ion signal is found while the ion yield is comparable [Figs. 1(b) and 1(c)] [20]. The structure exhibits a strong dependence on the laser excitation frequency: for a photon energy of 13 190 cm^{-1} no quantum interference is observed, and the ion yield at delay times $\lesssim 1$ ps is somewhat increased if compared to the one at large pulse separations ["shoulder structure," Fig. 1(b)]; in contrast, at an energy about 12 984 cm^{-1} the quantum interference structure appears again, although it decays within approximately 1.5 ps [Fig. 1(c)].

In order to understand these findings, one has to recall the results from cw-laser-induced fluorescence spectroscopy [Fig. 2(a)]. Absorption spectra of alkali-doped helium clusters are broadened to the blue by several tens of wave numbers [6,21]; the amount of broadening and the asymmetric line shape is well understood [6]. By proper choice of the excitation frequency, excited p states with different alignment (Σ- and Π-type states) with respect to the clusters surface can be populated [6,9]; this behavior applies in general to atoms residing on surfaces [22]. Figure 3 illustrates schematically the potential diagram of the ground state and low lying excited states of the K-He complex: the purely repulsive upper Σ state (which obtains its repulsive nature from the strong overlap of the

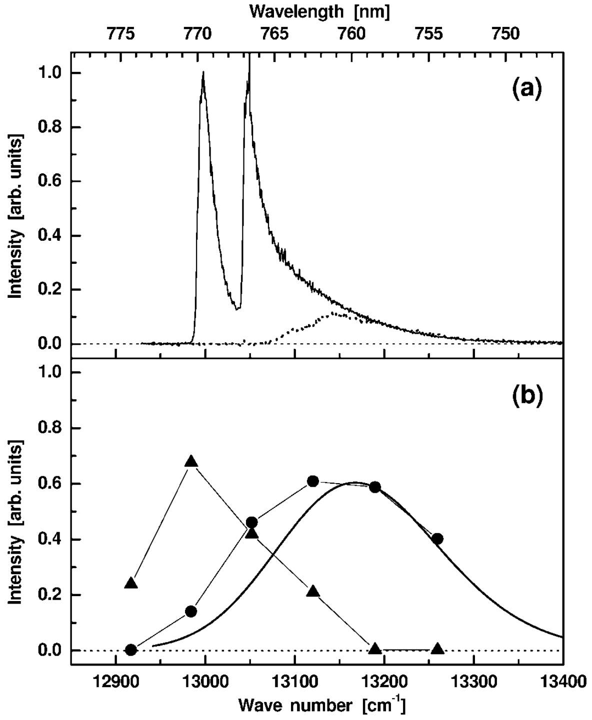

FIG. 2. (a) Absorption spectrum of potassium attached to helium droplets, as recorded with a cw laser [21]. The dotted line represents the absorption spectrum of those atoms which desorb and then emit in the gas phase (Σ excitation) [31]. (b) The solid circles give the integral of the shoulder at about 0.5 ps delay time [Fig. 1(b)] normalized to the asymptotic ion yield, the triangles depict the amplitude of the quantum interference [Fig. 1(c)] normalized the same way. The solid curve is a convolution of the dotted curve in the absorption spectrum (a) with the spectral profile of the fs laser.

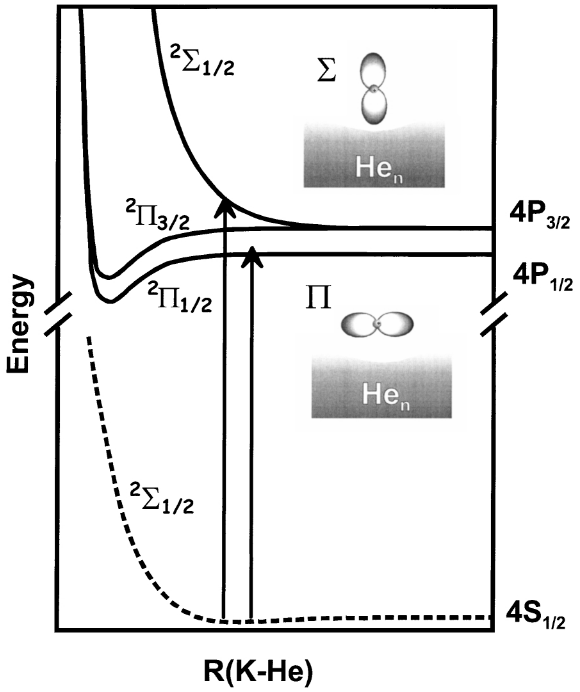

FIG. 3. Schematic potential energy diagram of the K-He complex illustrating different alignments of the excited p orbital with respect to the helium (Σ and Π states, respectively).

potassium p-electron distribution with the helium) requires blueshifted transition frequencies compared to the less overlapping Π state which is preferentially populated by excitation frequencies around the unperturbed potassium $s \rightarrow p$ transition [23]. Note, however, that the femtosecond laser used in our pulsed experiment has a large spectral width of approximately 175 cm^{-1}. Therefore the total absorption profile is considerably broader than the $p_{1/2}$, $p_{3/2}$ splitting. Nevertheless, even this broad structure allows one to differentiate between Σ and Π excitation by choosing laser frequencies at about 13 200 and 13 000 cm^{-1}, respectively, yielding the behavior displayed in Figs. 1(b) and 1(c): Evidently, the shoulder structure in Fig. 1(b) is characteristic of the Σ excitation, while the brief persistence of quantum interference shown in Fig. 1(c) is a consequence of Π excitation. This argument can be strengthened further [cf. Fig. 2(b)]: the spectral shape of the "shoulder" intensity is quite close to the (convoluted) absorption spectrum of the desorbed K atoms (i.e., Σ excitation), while the quantum interference pattern appears mainly at the laser photon frequencies characteristic for Π excitation. Apparently Σ excitation results in a strong reaction of the He surface, immediately destroying the coherence of the initial $4p$ state, while the Π state allows this coherence to persist for some time.

It is now interesting to compare this behavior to the results of other groups. For Σ excitation, Scoles and coworkers found a "direct" desorption of the chromophore from the surface with a lifetime of $\approx$70 ps [9]. In our experiment we probed the dynamics of the system at much shorter times before the adatom desorbs. Assuming a rigid [24] He$_N$ cluster, a typical vibrational frequency of a potassium atom is of the order of 2×10^{11} s^{-1} [6] which is slow compared to the time scale under study here. This suggests that because of the relatively heavy mass of the potassium atom it is the helium environment which rapidly backs away upon K-atom excitation. The extension of the shoulder structure in Fig. 1(b), approximation 1 ps, thus represents the analog of the expansion time of the bubble which is created in bulk superfluid helium upon the injection of a free electron. Applying a hydrodynamic model, Rosenblit and Jortner [25] obtained 3.9 ps for the expansion of bubbles as large as 17 Å. For alkali atoms the change in bubble radius is considerably less pronounced (e.g., from 5 Å for ground state Na atoms [19] to 9 Å in the direction of the p orbital in its first excited state [26–28]; for K atoms we may assume a similar behavior: the ground state bubble radius is 6 Å [28]). Using these radii in the hydrodynamic model [25] an expansion time of 1 ps is obtained, coinciding with the result of our measurements. We also note that similar effects exist in solid hydrogen: cage expansion times were measured to be 1.5 ps [29] when exciting Rydberg states in implanted NO. In addition, for this system the authors found no recurrence of the expanded cage structure. This is in agreement with the behavior in our K-He spectrum, as shown in Fig. 1(b), which clearly shows a monotonic decrease of the ion intensity. Also, apparently the helium environment, being forced into the new conformation, does not respond with noticeable oscillations. Finally, the absence of any interference structure in Fig. 1(b) demonstrates the strong perturbation from the surrounding helium on the coherently excited potassium doublet. Phase correlation is lost within 200 fs; shorter times cannot be accessed due to the strong pump-probe autocorrelation (grey shaded region in Fig. 1). A quantitative explanation for the detailed shape of the shoulder structure does not yet exist; it might, however, be suspected that it will be found in the influence on the photoexcitation/ionization by the changing optical properties of the K-He complex during the $\approx$1 ps rearrangement of the helium environment.

A quite different behavior is found [Fig. 1(c)] if lower transition frequencies are selected. Excitation at 12 984 cm^{-1} populates the Π configuration and results in a much less perturbed excited potassium because the p-electron distribution is expanded parallel to the helium surface. The shoulder structure in the average ion yield seen in Σ excitation is practically absent in Π excitation [30], and oscillations can be found up to delay times of $\approx$1.5 ps. This finding provides direct information on the coherence time of the system. The fluctuating helium environment causes the shapes and potential levels to fluctuate. Therefore, the phase information is lost due to the spread of transition frequencies. If we simply take the K-adsorbate excited state linewidth [20 cm^{-1}, cf. Fig. 2(a)], we arrive at a characteristic damping time of 10 ps. In contrast, the rapid oscillations [Fig. 1(c)] disappear much more quickly within about 1.5 ps, suggesting that even in the weakly interacting Π conformation the phase coherence is strongly disturbed by the presence of the helium cluster.

In conclusion, we have demonstrated that the femtosecond pump-probe technique applied to doped large helium clusters provides a novel tool to probe such complex systems. It allows one to follow their properties and short-time dynamics in real time. Although it has not played a special role in our discussion, it is worth recalling that the ^{4}He clusters in this experiment are known to be superfluid, constituting an extremely weak interacting medium. Apparently, adatom coherence phenomena are a particularly sensitive probe even for the very weak interaction with a superfluid rare gas surface. It might certainly be interesting to apply this method also to the normal-fluid ^{3}He clusters to find out whether a fingerprint of superfluid behavior could be extracted in this way.

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