

# Femtosecond Spectroscopy of Potassium-Doped Superfluid Helium Droplets

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Superfluid helium droplets are doped with potassium atoms forming a complex where the metal atom is weakly bound to the surface of the cluster. The dynamics of this system upon electronic excitation of the metal atom is probed by means of femtosecond pump-probe spectroscopy. Different effects are observed depending on the alignment of the potassium's upper p-orbital. A transition into the  $\Pi$ -type state leads to ultrafast quantum interferences. Owing to the broadening of the potassium's absorption in the helium environment, the lifetime extremely shortens ( $\approx 1.5$  ps) compared to the excited free potassium atom. Exciting a  $\Sigma$ -type state, the strong repulsive interaction with the helium surface comes into play. The corresponding response time of the helium environment is measured.

## 1 Introduction

Recently, doped helium clusters have received considerable interest, both in experiment and theory [1, 2]. Their unique properties make these cold ( $T = 370$  mK [3]) droplets an ideal tool for a variety of investigations, e.g.:

- the superfluid property of helium [4, 5];
- ultracold and weakly perturbing matrix for high resolution molecular spectroscopy [1];
- weakly bound complexes like e.g. high-spin states of alkali molecules [6, 7];
- bubble formation in the superfluid helium environment investigated by attaching metal atoms [8-10].

Besides this, dynamic effects on alkali-doped large helium clusters have been studied by Scoles et al. [11] using picosecond lasers. These investigations cover a time domain of several tens to hundreds of picoseconds. With the availability of lasers generating pulses in the sub-100 fs time domain, however, real-time spectroscopy now allows us to probe even the coherent dynamics of such systems down to a few 10fs. A first study of this kind is the topic of this report.

In the brief history of femtosecond lasers many molecules and clusters have been studied following the pioneering work

of A.H. Zewail and his group [12, 13]. Due to their relatively easy experimental as well as theoretical handling, alkali systems can act as excellent model systems ([14] and refs. therein). A variety of ultrafast phenomena such as wave packet propagation [15], intramolecular vibrational redistribution [16], and photodissociation have been observed. Coherent phenomena were first seen in cesium dimers [17] and, very recently, quantum coherence was detected in potassium and cesium atoms [18, 19].

In this report we use the coherently excited potassium atom to probe the ultrafast coherent dynamics in a  $K-He_N$ -system ( $N \approx 5000$ ), or, from point of view of atomic physics, we like to study how fast the helium cluster will perturb the atomic excited state coherence. This experiment, therefore, establishes a nice link between atomic and condensed matter physics, providing a novel and efficient tool for probing the coherence and excited state wave packet dynamics of such rather complex systems.

## 2 Experimental

The experimental setup for generating a metal-doped helium cluster beam is similar to the one described earlier for cw-spectroscopy [10, 20]. The clusters are generated in a supersonic expansion of helium gas from a cold nozzle at high stagnation pressure. They are doped with single potassium

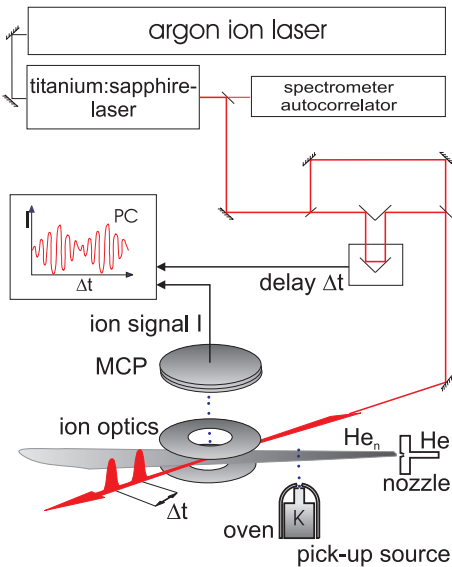


Figure 1: Experimental setup. for real-time spectroscopy of alkali-doped superfluid helium clusters. Explanations see text.

atoms by sending the beam through a heated oven which provides the necessary K-vapor pressure. The metal atoms are captured in flight. The energy involved in this collision process is dissipated by evaporative cooling of the helium cluster. Hence, the helium droplet rapidly returns to its temperature of 370 mK [3]. From previous work [8, 21] it is known that alkali atoms reside in a shallow dimple on the clusters surface.

In a separate vacuum chamber located further downstream, the doped cluster beam intersects at right angles with the ultrashort pulses from a modelocked titanium-sapphire laser. This laser provides light in the spectral range of interest ( $12500\text{ cm}^{-1}$ –  $13300\text{ cm}^{-1}$ ) and is tuned to the  $4p \leftarrow 4s$  electronic transition of the K chromophore. Assuming  $\text{sech}^2$  shaped pulses, a pulse duration of 90 fs (FWHM) has been estimated from interferometric autocorrelation traces. In the wavelength region of interest, the Fourier-limited spectral width of these pulses is approx.  $175\text{ cm}^{-1}$  (FWHM). This enabled coherent excitation of the 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. The ions generated by three-photon ionization of the K-atoms are accelerated perpendicularly to both, cluster and laser beam and are detected in a channeltron detector (see Fig. 1).

### 3 Results

In a pre-experiment we probed free potassium atoms, which evaporated effusively from the pick-up oven (Fig. 2a). The ion intensity displays the well known quantum interference

structure (oscillations at the optical period of 2.56 fs), as well as amplitude beats (period of 576 fs) which correspond to the fine structure splitting of the 4p-state [18, 19]. In our experiment we were able to follow this pattern for pump-probe delays exceeding 100 ps.

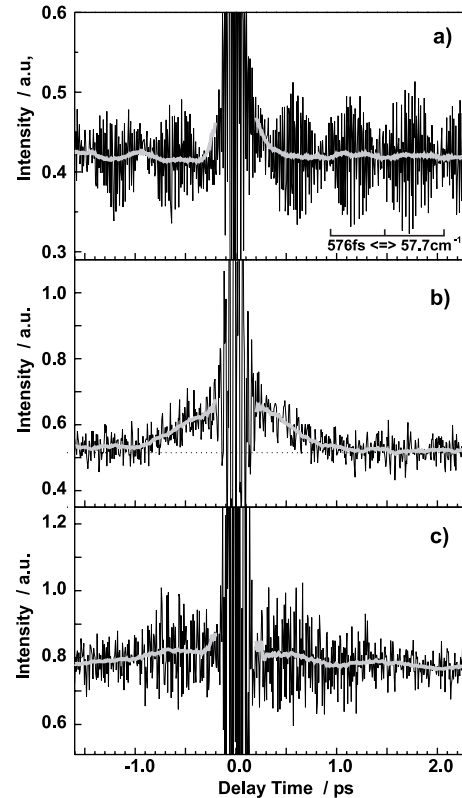


Figure 2: (a) Ion intensity from three-photon ionization of gas-phase potassium atoms as a function of delay time, obtained by exciting the effusive beam from the pick-up cell. The rapid oscillation stems from quantum interferences, the beat structure represents the fine structure splitting of the intermediate  $4p_{1/2, 3/2}$  state. The thick grey line gives the averaged intensity. (b) Same as above but exciting potassium-doped helium clusters. The excitation frequency is  $13190\text{ cm}^{-1}$ . In (c) the laser is tuned to  $12984\text{ cm}^{-1}$ , where quantum interferences are visible. The broad grey bar covers the autocorrelation around zero delay.

However, when probing potassium-doped helium clusters, a quite different time structure of the ion signal is found while the ion yield is comparable (Fig. 2b, c). The structure exhibits a strong dependence on the laser excitation frequency: for a photon energy of  $13190\text{ cm}^{-1}$  no quantum interference is observed, and the ion yield at delay times  $\leq 1\text{ ps}$  is somewhat increased if compared to the one at large pulse separations. A weak “shoulder structure” appears, as seen in Fig. 2b).

In contrast, at an excitation energy of  $12984\text{ cm}^{-1}$  the quantum interference structure appears again, although it decays within approximately 1.5 ps (Fig. 2c).

## 4 Discussion

To understand these findings one has to recall the results from cw-laser-induced fluorescence spectroscopy. The absorption spectra of alkali-doped helium clusters are broadened to the blue by several tens of wavenumbers [8, 22]. The amount of broadening and the asymmetric line shape is well understood on the basis of the bubble formation mechanism [8]. By proper choice of the excitation frequency, excited p-states with different alignment ( $\Sigma$ - and  $\Pi$ -type states) with respect to the clusters surface can be populated [8, 11]. This behavior applies in general to atoms residing on surfaces [23].

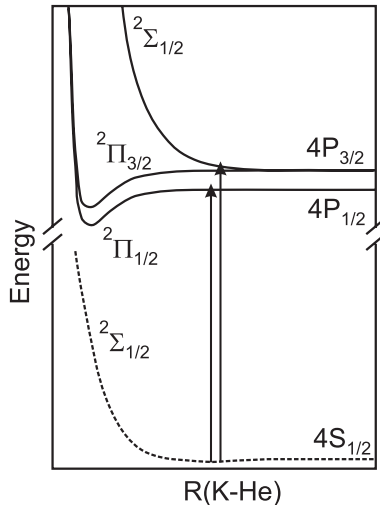


Figure 3: Schematic potential energy diagram of the K-He complex for the relevant transition  $s \rightarrow p$ .

Fig. 3 illustrates schematically the potential diagram of the ground state and low lying excited states of the K-He Dimer. The purely repulsive upper  $\Sigma$ -state requires blue-shifted transition frequencies compared to the less-overlapping  $\Pi$ -state which is preferentially populated by excitation frequencies around the unperturbed potassium  $s \rightarrow p$  transition. The strongly repulsive  $\Sigma$ -excitation results in a direct desorption of the chromophore from the surface and an ensuing fluorescence emission by the free atom.

The femtosecond laser pulses used in our pulsed experiment have a large spectral width of approx.  $175 \text{ cm}^{-1}$ . Therefore, the total absorption profile, (squares in Fig. 4a) can not resolve the  $P_{1/2}, P_{3/2}$  splitting. It provides a single broad maximum, in close agreement with a convolution of the cw absorption spectrum [22] with the spectral laser profile.

Nevertheless, even this broad structure allows us to differentiate between  $\Sigma$ - and  $\Pi$ -excitation by choosing laser frequencies around  $13200 \text{ cm}^{-1}$  and  $13000 \text{ cm}^{-1}$ , respectively. The observed behavior is displayed in Fig. 2b) and 2c). The “shoulder structure” in Fig. 2b) is characteristic of the  $\Sigma$ -excitation, while the brief persistence of quantum interfer-

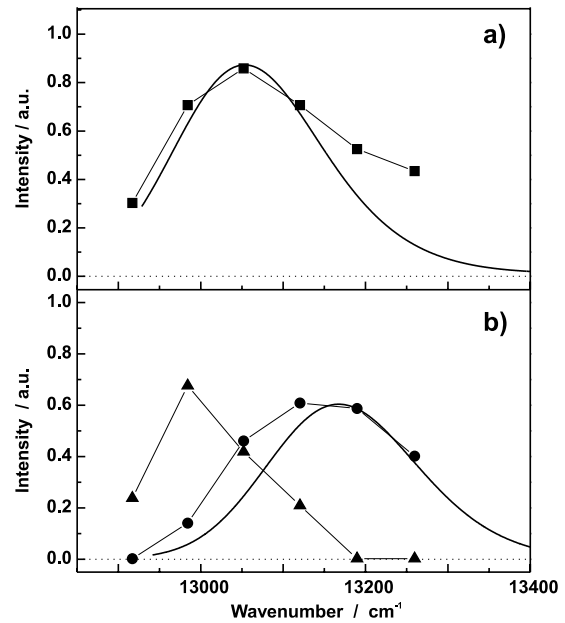


Figure 4: a) Squares: asymptotic ion rate for long delay times; solid line: convolution of total absorption spectrum [22] with Gaussian function of  $175 \text{ cm}^{-1}$  FWHM. b) Full circles give integral of shoulder around  $0.5 \text{ ps}$  delay time (Fig. 2b)) normalized to asymptotic ion yield, triangles depict amplitude of the quantum interference (Fig. 2c)) normalized the same way. Solid curve: convolution of the dotted curve in absorption spectrum [22] with Gaussian function of  $175 \text{ cm}^{-1}$  FWHM.

ence shown in Fig. 2c) is a consequence of  $\Pi$ -excitation.

This argument can be strengthened further (c.f. Fig. 4b)). The spectral shape of the “shoulder” intensity is quite close to the (convoluted) absorption spectrum of the desorbed K atoms (i.e.,  $\Sigma$ -excitation), while the quantum interference pattern appears mainly at the laser photon frequencies characteristic for  $\Pi$ -excitation. Apparently  $\Sigma$ -excitation results in a strong reaction of the He surface (see Fig. 5), immediately destroying the coherence of the initial  $4p$  state, while the  $\Pi$  state allows this coherence to persist for some time.

The absence of any interference structure outside the autocorrelation region demonstrates the strong perturbation from the surrounding helium on the coherently excited potassium doublet. Phase correlation is lost within  $200 \text{ fs}$ ; shorter times can not be accessed due to the strong pump-probe autocorrelation.

A different behavior is found (Fig. 2c)) if lower transition frequencies are applied. Exciting the system at  $12984 \text{ cm}^{-1}$  populates the  $\Pi$ -configuration and results in a much less-perturbed excited potassium. It is caused by expansion of the p-electron distribution parallel to the helium surface (see Fig. 5). The “shoulder structure” in the average ion yield seen in  $\Sigma$ -excitation is practically absent in  $\Pi$ -excitation, and coherent oscillations can be found up to delay times of  $\approx 1.5 \text{ ps}$ . This provides direct information on

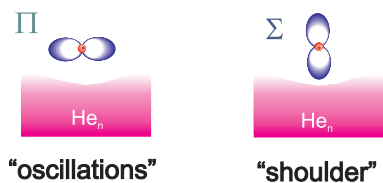


Figure 5: Illustration of different alignments of the excited p-orbital of the K-He-complex with respect to the helium surface.

the influence of the helium environment on the coherence of the system. This short drop-off within 1.5 ps suggests that even in the weakly interacting  $\Pi$ -conformation the phase coherence is significantly disturbed by the helium cluster.

## 5 Conclusions

Summarizing, we have shown that the femtosecond pump-probe technique applied to doped large helium clusters provides a novel tool to probe such complex systems. It allows to follow the properties and short-time dynamics of size-limited superfluid aggregates in real time. In particular, it probes the ultrafast perturbation and destruction of atomic coherence by a large superfluid entity. In conclusion, adatom coherence phenomena are apparently a particularly sensitive probe even for the very weak interaction with the superfluid rare gas surface.

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