Femtosecond time-resolved Rydberg wave-packet dynamics in the two-electron system calcium

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(Received 10 February 1998)

We have investigated the radial Rydberg wave-packet dynamics in the two-valence-electron atom calcium by femtosecond pump-probe spectroscopy. The classical periodic motion of the Kepler electron as well as the quantum mechanical revival structure were observed when employing the phase sensitive detection technique. Preliminary results are reported on Rydberg wave-packet autoionization under the influence of an isolated excitation of the remaining outer core electron. [S1050-2947(98)02507-4]

PACS number(s): 32.80.Rm, 32.80.Qk, 32.80.Dz

I. INTRODUCTION

The study of radial Rydberg wave-packet dynamics in atoms has attracted considerable interest from experimentalists and theoreticians, because both classical and quantum mechanical properties are seen in the dynamics [1]. Coherent excitation of high lying electronic eigenstates with low angular momentum by a spectrally broad ultrashort laser pulse leads to the formation of a radial Rydberg wave packet. With the Rydberg wave packet properly localized in the spatial coordinates, the classical aspects of its temporal evolution can be visualized by an ensemble of electrons moving on Kepler trajectories around the nucleus. Due to the dispersion resulting from the anharmonicity of the energy spacings between the coherently coupled levels, the initially localized wave packet will spread out. Quantum mechanically, however, it can be shown that, after a given time, the Rydberg wave packet will recur again. In one-electron atoms, classical as well as quantum mechanical aspects have been extensively studied experimentally [2–6] and theoretically [7–9]. The results of these investigations have facilitated the study of more complex systems, for instance atoms with two valence electrons.

The correlation between the two valence electrons opens up a wide range of new physical effects. The most significant difference, as compared to one-electron atoms, is the existence of doubly excited states leading in general to autoionization and perturbation of Rydberg series. One of the striking features of two correlated electrons is the possibility to control the one-electron dynamics by driving the other electron with an external laser field. A pioneering experiment in that context was performed by Cooke *et al.* [10]. They showed that the photoionization cross section of highly excited states can be strongly enhanced by excitation of a Rydberg state and a subsequent excitation of the remaining isolated ionic core. This stepwise excitation leads to efficient autoionization of the two-electron atom. Further experiments along these lines were reported, for instance by Jones and Bucksbaum [11], van Druten and Muller, [12] and Gallagher and co-workers [13,14]. The first who proposed applying this excitation scheme for controlling atomic wave-packet dynamics were Wang and Cooke [15], while the first experimental realization was reported by Story, Duncan, and Gallagher [16], who investigated the cross section dependence for autoionization of a Rydberg wave packet upon the wavelength of the core-resonant laser. The influence of an isolated core excitation on the Rydberg wave-packet dynamics in the weak field limit [17], as well as in the case of a strongly driven core resonance [18,19], was studied theoretically, and led to predictions of observable effects.

Here we report on time-resolved experiments to study electronic Rydberg wave-packet dynamics in atomic calcium. Spectroscopically, this earth alkaline atom is well understood [20–22], but so far there have been no reports on time-resolved studies of electronic wave-packet dynamics in calcium. With intrinsically spectral broad femtosecond laser pulses, we coherently excite several low lying electronic eigenstates around $n=20$, thus forming a Rydberg wave packet. This selection of coherently coupled levels allows the detection of the long term evolution, and we expect to observe very early revivals of the Rydberg wave packet. Furthermore preliminary results on Rydberg wave-packet autoionization by an isolated excitation (weak laser field) of the remaining outer core electron are discussed.

II. EXPERIMENT

In our experiment, we combine different experimental methods. Femtosecond laser techniques are used together with ion and electron time-of-flight (TOF) spectroscopy and atomic beam techniques to study the dynamics of electronic excitations.

An effusive Ca beam is prepared by heating calcium grains up to 1000 K in a differentially pumped oven chamber. The oven chamber is connected via a 1-mm skimmer to the high-vacuum detection chamber which houses the TOF spectrometer. The interaction region of the atomic beam with the laser beam is placed between two voltage controlled capacitor plates. The released ions and photoelectrons are detected by mass-selective ion TOF spectroscopy, and by energy-resolved electron spectroscopy, respectively. In order to detect the formed ions, a small extraction field is applied, whereas the electrons are measured without any additional electric field in the interaction region. The fs-laser pulses are generated by a regeneratively amplified 1-kHz Ti:sapphire laser system based upon chirped pulse amplification (CPA) with output pulses of 900-μJ energy and 80-fs pulse duration at a center wavelength of $\lambda_0=816$ nm. Employing a 1-mm-thick BBO crystal, the 816-nm laser pulses are efficiently frequency doubled. With these $\lambda\approx 408$ nm photons

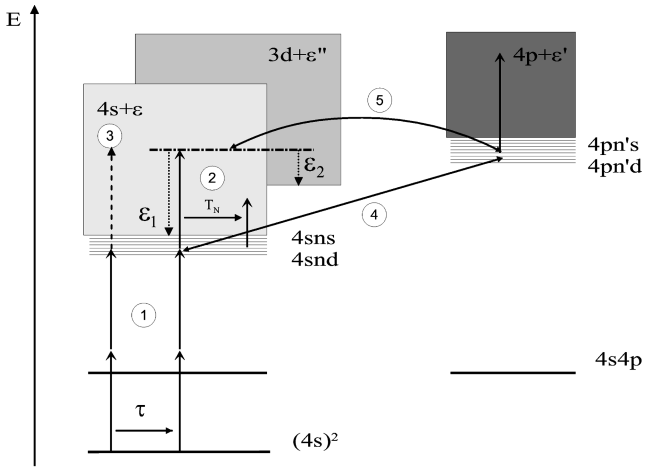

FIG. 1. Excitation scheme of atomic calcium. Illustrated are (1) the two-pulse phase sensitive pump-probe detection scheme, (2) the postionization method, (3) the process of direct ionization, (4) the core-resonant excitation $Ca^*(4snd) \rightarrow Ca^{**}(4pnd)$, and (5) the configuration interaction leading to autoionization. The kinetic energies of the electrons released in different ionization channels are denoted with ε_i.

we then excite the electronic Rydberg states via a two-photon process, and form a Rydberg wave packet. For the pump-probe experiment the 408 nm ultrashort laser pulse is split into two coherent, temporally controlled laser pulses in a Michelson-type setup. Since we experienced difficulties in the detection of Rydberg wave packets in a conventional pump-probe experiment because of the low ionization probability of Rydberg states for ultraviolet or visible photons, we applied the phase sensitive detection technique introduced in Refs. [23–25] to our measurements.

In the phase sensitive technique, each of the temporally controlled two pump laser pulses generates an identical wave packet. If the time delay τ between these two wave packets ψ_1 and ψ_2 is an integer multiple of the electron wave-packet orbiting time, these wave packets overlap in the vicinity of the core, resulting in constructive or destructive interference $|\psi_1+\psi_2|^2$, and therefore causing a change of the Rydberg state populations. This change is reflected in the detection channel, i.e., in the ionic continuum. In particular, this interference signal is modulated by the average excitation frequency ω_{mod} which excites the Rydberg states and forms the wave packet. In a two-photon excitation process the modulation frequency is given by $\omega_{\mathrm{mod}}=2\omega_{\mathrm{laser}}$. If there is no temporal overlap of the two wave packets, no interferences will occur, and the total Rydberg state population $|\psi_1|^2+|\psi_2|^2$ will stay constant. The essential point in our data processing is to filter out the squared amplitudes $(A_{\mathrm{mod}})^2$ of the contributions to the signal with the given modulation frequency $A_{\mathrm{mod}}\sin(\omega_{\mathrm{mod}})$. Consequently, every peak in the signal belongs to a (partial) return of the wave packet to the core. Thus we directly monitor the time evolution of the wave packet.

Experimentally we have employed the phase sensitive detection technique in two different schemes (see Fig. 1). One possibility is to excite the wave packet in a two-photon process with the first pump laser pulse, while the second pump laser pulse creates the second wave packet and simultaneously transfers the actual population by absorption of an additional photon into the continuum. This (2+1)-photon ionization process can be enhanced by exciting an autoionizing resonance. However, because of the spectrally broad fs-laser pulses not only three-photon but also two-photon direct ionization processes can contribute to the measured ionization yield, leading to an unwanted background signal. This is why we applied a second approach with a three-pulse sequence in the phase sensitive technique. As before, two temporally controlled pump laser pulses generate the interfering Rydberg wave packets, but now a third time-delayed probe laser pulse photoionizes the Rydberg population. In order to generate these probe pulses we couple out about 50% of the available infrared pulse energy at $\lambda_0 \approx 816$ nm entering the compressor of the CPA laser system, thus providing laser pulses with approximately 200-ps duration. These long ps-laser pulses are subsequently delayed by about 50 ns with respect to the femtosecond excitation pulses. The pulse duration of 200 ps was sufficiently long, as compared to the round-trip time of the Rydberg wave packet, in order to extract a fair amount of the (after 50 ns) remaining Rydberg population. In our experiments we utilized laser postionization and not electric field ionization because of the chosen low principal quantum number n_0 of the Rydberg wave packet. The advantage of the postionization method employed is that within the time delay of 50 ns all the background signal from direct ionization processes disappears, so that a background-free phase sensitive signal can be measured.

Figure 2 shows TOF spectra for the produced ions (a) and the corresponding electrons (b). Ion pump-probe spectra (see Fig. 3) revealed a signal variation resulting from Rydberg wave-packet dynamics only when we used the ion signal peak arising from laser postionization (B). In contrast to that, all electron pump-probe spectra (see Fig. 4) are of comparable quality, no matter which electron signal peak was chosen to record the dynamics [see Fig. 2(b)]. Consequently, when measuring the background-free electron signal, the laser postionization is not necessarily required.

III. RESULTS AND DISCUSSION OF ONE-ELECTRON RYDBERG WAVE-PACKET DYNAMICS

In a two-photon stepwise excitation of $Ca(4s^2)\ ^1S_0$ using linearly polarized (parallel to the TOF axis) fs-laser pulses, $4sns$ and $4snd$ states are excited, which lead to the generation of radial Rydberg wave packets with dominant d character. With a center wavelength of $\lambda \approx 408.5$ nm atomic Rydberg states at a mean principal quantum number of $n_0 = 19.75$ are coherently excited. Considering the two-photon bandwidth $\Delta\lambda = \sqrt{2}\,\Delta\lambda_{\mathrm{laser}}$, electronic states ranging from $n_{\mathrm{min}}=17$ to $n_{\mathrm{max}}=22$ are expected to contribute to the formation of the Rydberg wave packet. In Figs. 3 and 4, pump-probe spectra are shown for ion and electron detection, respectively. The inset in both figures gives the corresponding fast Fourier transform (FFT).

The ion pump-probe spectrum, measured by applying the laser postionization technique, shows a signal variation which reflects the dynamics of the Rydberg electron wave packet, as proven by the frequencies obtained in the Fourier transformation. Note that the energy levels are slightly

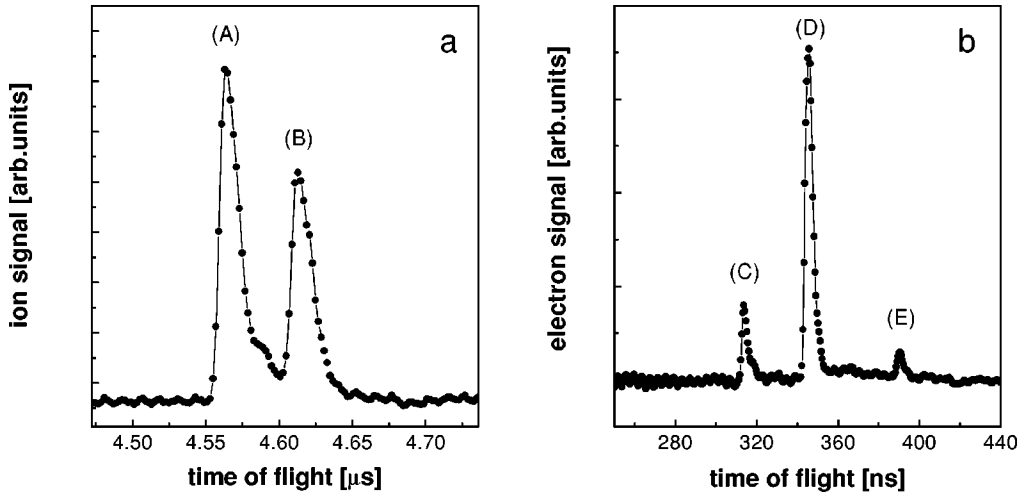

FIG. 2. Typical time-of-flight (TOF) spectra of formed ions (a) and the corresponding electrons (b). The Ca^+ peak labeled (A) must be distinguished from the Ca^+ peak labeled (B), which is due to laser postionization. The labels (C) and (D) in the electron TOF spectrum belong to the electron peaks resulting from ionization into the $4s$ and $3d$ continua, respectively. The electrons (E) originate from laser postionization.

shifted due to the Stark effect ($\Delta E_s = \frac{3}{2}\, nkF$, k is the parabolic quantum number and F is the applied electric extraction field), although for our experimental conditions this effect ($\Delta E_s < 2\ \mathrm{cm}^{-1}$) does not significantly change the dynamical evolution. Because of the integral detection of the total ion yield, which does not allow one to distinguish different ionization channels, the observed Rydberg dynamics still suffers from a disturbing background signal and an insufficient signal-to-noise level. In order to separate different ionization channels and to improve the signal-to-noise ratio of the pump-probe spectra, we carried out electron measurements. The detection of electrons has the additional advantage that no Stark shift and mixture of l states have to be taken into account.

A signal variation similar to that seen in the ion measurement is also observed in the electron pump-probe spectrum. The full and fractional revivals, however, are much better resolved in the electron measurement. We believe that this difference is due to the slightly different excitation wavelength compared to the ion measurement, which leads not only to an excitation of a different n_0 but also to a more symmetric population of the coupled Rydberg states. Further analysis of the electron pump-probe spectrum reveals the classical period of the orbiting Kepler electron to be 1200 fs. This time interval, however, can only be seen at the first revival and then successive revivals of the wave packet. Additionally, at a pump-probe delay time of about 3200 fs, the half revival is clearly visible. The wave packet has split into

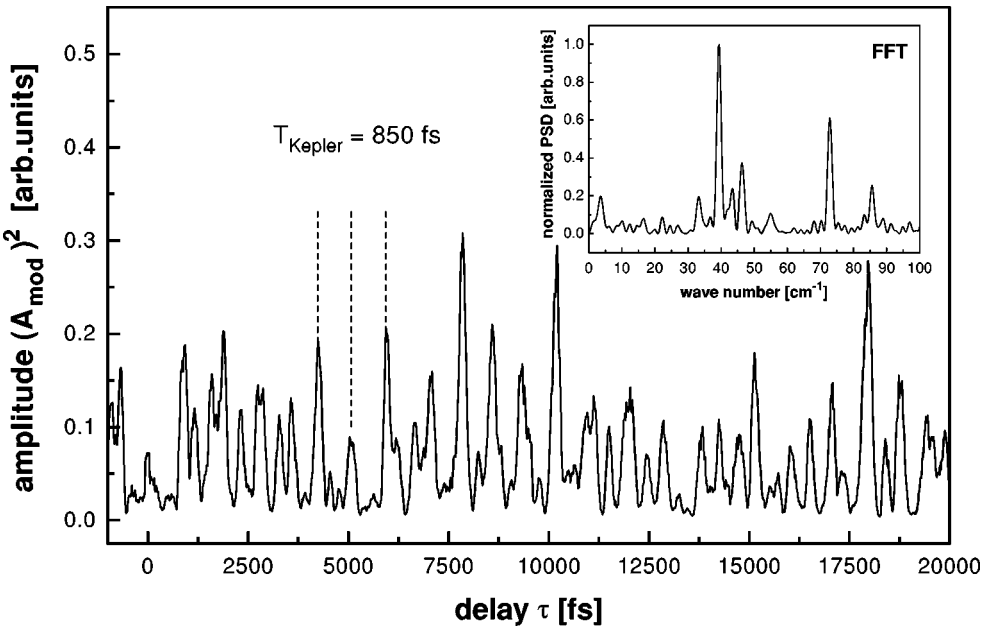

FIG. 3. Ion pump-probe spectrum showing the Rydberg wave-packet dynamics. The spectrum is recorded by employing the phase sensitive detection technique on the Ca^+ peak from laser postionization. The inset shows the fast Fourier transform (FFT) with peaks reflecting the energy differences of the coupled Rydberg states.

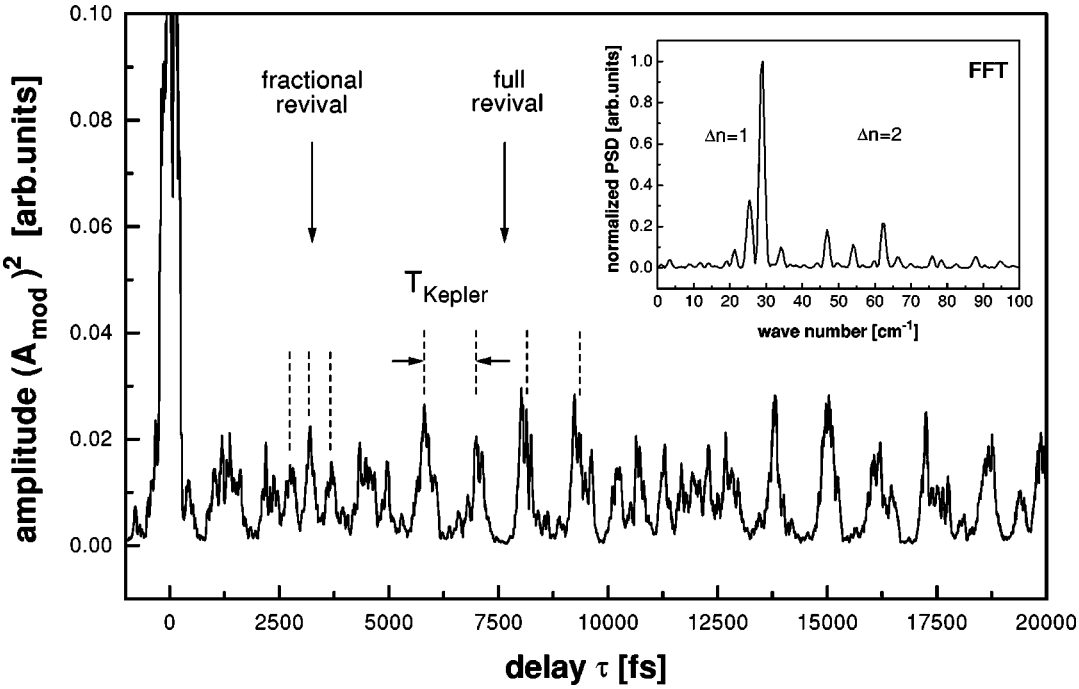

FIG. 4. Electron pump-probe spectrum showing the Rydberg wave-packet dynamics. Besides the Kepler period, the spectrum also shows additional structures resulting from fractional revivals with an excellent signal-to-noise ratio. The FFT reveals spectroscopic data that are in good agreement with spectroscopically determined energy differences (see also Table I).

two parts, thus doubling the beat frequency. With the given experimental parameters we expect a Kepler period $T_{\mathrm{cl}} = 2\pi n_0^3$ of 1160 fs for $n_0 = 19.75$, and a full revival at 7640 fs as calculated from $T_{\mathrm{rev}} = n_0 T_{\mathrm{cl}}/3$ [9]. The experimental results are in good agreement with these theoretical predictions. The FFT of the electron spectrum yields information on the energy differences of the coherently coupled Rydberg states. The FFT frequencies can be assigned to the coupling of states with $\Delta n = 1$ and 2. This result shows again that spectroscopic data can be derived from time-resolved measurements [26]. A comparison of the FFT frequencies with available spectroscopic data shows excellent agreement (see Table I).

It should be noted that the FFT results of the separately measured ion and electron pump-probe spectra cannot be compared, because of long term thermal drifts of the center wavelength of our fs-laser system. These drifts can lead to an excitation of electronic states with different mean principal quantum number n_0. Unfortunately, simultaneous detection of electrons and ions is not possible with our current experimental setup.

TABLE I. The frequencies obtained by the fast Fourier transform of the electron pump-probe spectrum (see Fig. 4) can be assigned to energy spacings of coherently coupled states with $\Delta n = 1$ and 2. This shows that spectroscopic data can be derived simultaneously from time-resolved measurements.

Coupled states	Experimental result (cm^{-1})	Literature (cm^{-1})
$4s22d-4s21d$	25.97	25.20
$4s21d-4s20d$	28.90	28.88
$4s20d-4s19d$	33.67	33.44
$4s19d-4s18d$	—	39.39
$4s18d-4s17d$	46.86	46.53
$4s22d-4s20d$	53.91	54.08
$4s21d-4s19d$	62.55	62.32

Summarizing our observations, we find that the combination of the phase sensitive technique with femtosecond photoelectron spectroscopy is an ideal means to monitor both the classical and the quantum mechanical behavior of a Rydberg electron. Although for a better illustration the spectra in Figs. 3 and 4 are shown only up to 20-ps delay time, the wave-packet dynamics was detectable even for delay times as long as 80 ps without any loss of modulation depth. Moreover, by excitation of low-lying n states with femtosecond laser pulses an early observation of revivals is possible ($T_{\mathrm{rev}} \sim n^4$).

IV. ISOLATED CORE EXCITATION

When the Rydberg wave-packet dynamics is studied under the influence of a driven core resonance, the ionization probability depends sensitively on the intensity of the core-resonant laser. Two different experimental situations must be considered. On the one hand the core transition can be driven such that the induced Rabi oscillation ($\Omega_{Rabi} \sim \sqrt{I_{\mathrm{laser}}}$) between the core states matches the Kepler period of the electron wave packet. If both oscillations are synchronized with a relative phase such that the core is in its excited $4p$ state while the wave packet is localized at its outer turning point, then only the tails of the Rydberg wave packet will autoionize. The center of the wave packet is instead stabilized against autoionization for many cycles [18,27]. Consequently, a shaping of the wave packet takes place, which strongly reduces the spreading. The Kepler motion of the electronic wave packet will be observable for long propaga-

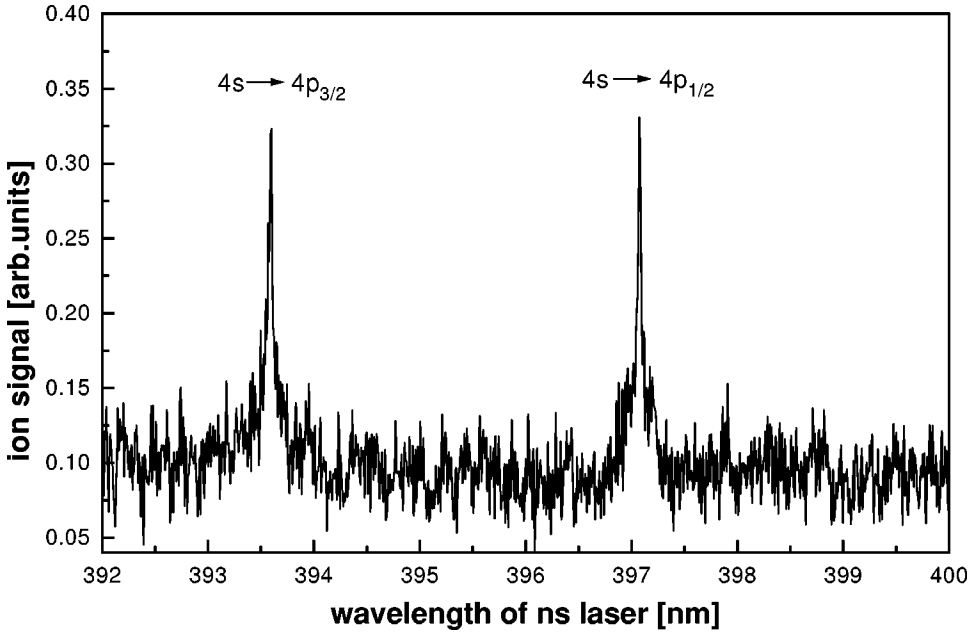

FIG. 5. Isolated core excitation. The formed Rydberg wave packets are autoionized by driving the $Ca^*(4snd) \rightarrow Ca^{**}(4p_{1/2,\,3/2}nd)$ core transition with a tunable ns laser. The two wavelengths found by tuning the ns-laser match exactly the known values for these transitions in the singly charged ionic system $Ca^+ \ ^2S_{1/2}$ (Ca II).

tion times. On the other hand, the Kepler and Rabi periods can be out of phase, if the intensity of the laser driving the core resonance is not properly chosen. If the core is excited, whenever the Rydberg wave packet is localized near the core, the significant overlap of both wave functions induces autoionization. Thus the Rydberg wave-packet motion vanishes within a few round trips.

Recently in a first experiment we observed the autoionization of Rydberg wave packets induced by the isolated core excitation $Ca^*(4snd) \rightarrow Ca^{**}(4pnd)$ in the weak field limit (see Fig. 5). A tunable nanosecond laser, resonant with the core transition, and the femtosecond laser which formed the Rydberg wave packet, were synchronized and brought to both temporal and spatial overlap. Since we used a ns laser to excite the core transition inducing the autoionization of the Kepler electron, a time-integrated signal was recorded, smearing out any temporal information on the wave packet dynamics. The wavelengths λ_1 and λ_2 of the observed two maxima in the ion signal match the excitation energies of the bound states $Ca^+(4s \rightarrow 4p_{1/2})$ and $Ca^+(4s \rightarrow 4p_{3/2})$, respectively. Thus at the low principal quantum number of $n=20$, the atomic system, representing a Ca^+ core with a quasifree—but still bound—Rydberg electron, already changes to the ionic configuration Ca II $^2S_{1/2}$.

V. CONCLUSION

In conclusion, we have reported on radial Rydberg wave-packet dynamics in the two-valence-electron atom calcium. The combination of photoelectron spectroscopy and phase sensitive detection with femtosecond laser pulses has proven to be ideal for revealing full information on the wave-packet evolution. Both the classical Kepler period and the quantum mechanical phenomenon of revivals have been observed. Owing to the observed long term evolution of the wave packet the Rydberg states, which form the electronic wave packet, could be determined from a fast Fourier transform. The autoionization of the Rydberg wave packet induced by an isolated core-resonant excitation was observed. This experiment shows that atomic calcium is an ideal system to investigate the correlation of two valence electrons.

During the course of submission, we became aware of a very recent work by Jones on the measurement of the electronic radial probability distribution of a $4snd$ wave packet in Ca by time-resolved isolated core excitation (ICE) [28]. In contrast to our experiments, he employed ICE to investigate the temporal evolution of the radial Rydberg wave packet by tuning the wavelength of the core transition. It should be noted that in Jones' work the temporally short ($\approx$500 fs) ICE laser was operated in the low intensity regime, thus avoiding any Rabi oscillations.

ACKNOWLEDGMENTS

The authors would like to thank A. Assion, T. Baumert, and V. Seyfried for many fruitful discussions. Theoretical support from B. Mecking and P. Lambropoulos has been most valuable. Financial support from the Deutsche Forschungsgemeinschaft through the DFG-Schwerpunkt ''Femtosekunden-Spektroskopie'' is gratefully acknowledged.

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