Dynamics of forced autoionization

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(Received 20 January 1999)

In this Rapid Communication we report on the autoionization dynamics of the $5d7d$ doubly excited state in barium in a static electric field. The different experiments and theory show Stark beatings in the autoionization process. Also it appears that the total spin of the two valence electrons plays a major role in the ionization dynamics. Absorption spectroscopy revealed the ionization dynamics near the core, while an atomic streak camera was used to record the time-dependent electron emission, probing the wave function when it is far from the core. Calculations based on multichannel quantum defect theory are compared to experimental data and we are able to predict the singlet-triplet mixing. [S1050-2947(99)51611-9]

PACS number(s): 32.80.Rm

An atom in a doubly excited state has two electrons populating levels that are different from the ground state. These excited states can couple to states in which one electron has relaxed to the ground state and the other carries all the energy. If the total energy shared by the two electrons exceeds the binding energy, the second electron is forced to escape; the doubly excited state has decayed by autoionization into a ground-state ion plus a free electron. If the total energy is less than the binding energy, the doubly excited state can only couple to bound Rydberg states. However, in the presence of a sufficiently strong electric field such Rydberg states couple to continuum states; the electric field introduces a saddle point in the core potential over which the electrons can escape (see Fig. 1). The process by which the doubly excited state couples to a Rydberg state, which in turn couples to the field-induced continuum, is known as forced autoionization [1].

In this Rapid Communication we investigate the dynamics of such a forced autoionization process in the alkaline-earth atom barium to learn more about the complex electron dynamics of a decaying two-electron system. Starting from the ground state ($6s^2$) the $5d7d$ doubly excited state is laser excited via the $5d6p$ laser-excited intermediate state. We studied the dynamics of the coupling to the $6s\epsilon k$ Rydberg series followed by the ionization of the Rydberg Stark states. The approach of our study is threefold. First we performed a high-resolution spectroscopy study. This conventional means of studying the system [2] yields dynamical information equivalent to optical pump-probe studies with short laser pulses [3]. In such a pump-probe study the pump pulse creates a Rydberg wave packet Ψ, and after a delay time τ a second wave packet is launched by the probe pulse. The interference of the two wave packets is measured. Since the Rydberg wave packet Ψ is a projection of the ground-state wave function on the Rydberg states, the launched wave packet $\Psi(t=0)$ is near the core. As a result both spectroscopy and pump-probe experiments yield information on the low-angular-momentum character of the wave packet near the core. With the help of the recently developed atomic streak camera were able to measure the outgoing electron flux with a picosecond resolution and thus probe the electronic wave function near the saddle point. Finally we applied a version of multichannel quantum defect theory (MQDT) [4,5] describing the dynamics probed by both types of experiments accurately.

We report on two remarkable findings on the forced autoionization dynamics of the barium $5d7d$ state. First, both the spectroscopy and the electron emission data showed a beating of the autoionization process. The angular-momentum degeneracy is lifted by the electric field. The resulting Stark states are coherently excited yielding an oscillation of the angular momentum (Stark beating) [6,11]. However, the dynamics as seen with both techniques is not the same since they probe different parts of the wave function. Second, the nature of the dynamics is somewhat more complex than sketched above since also the spin of the two electrons is involved. The spin of the outgoing electron is antiparallel or parallel to the spin of the electron that is in the ground state Ba^+ ($6s$). We find that the dynamics of electron emission in the two spin channels is dramatically different. While direct ejection of the electron results mostly in a singlet state, the triplet emission is dominant for longer times.

Both experiments were performed in a vacuum chamber with a background pressure of 5.0×10^{-7} Torr. In our spectroscopy experiment, revealing the electron dynamics near

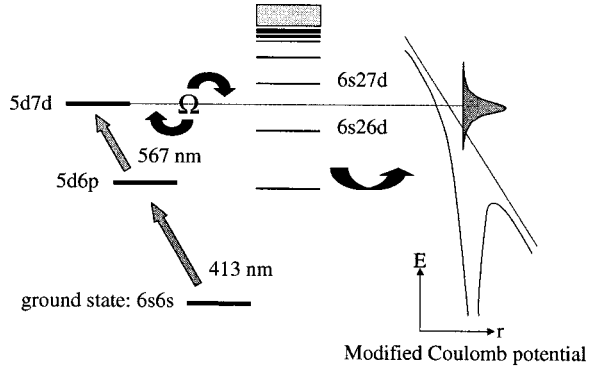

FIG. 1. The process of forced autoionization as studied in Ba. A doubly excited state is created by means of two consecutive laser pulses. The doubly excited state ($5d7d$) couples strongly to the $6snd$ Rydberg states through configuration interaction. These states in turn are coupled to a continuum in a strong electric field and can therefore autoionize.

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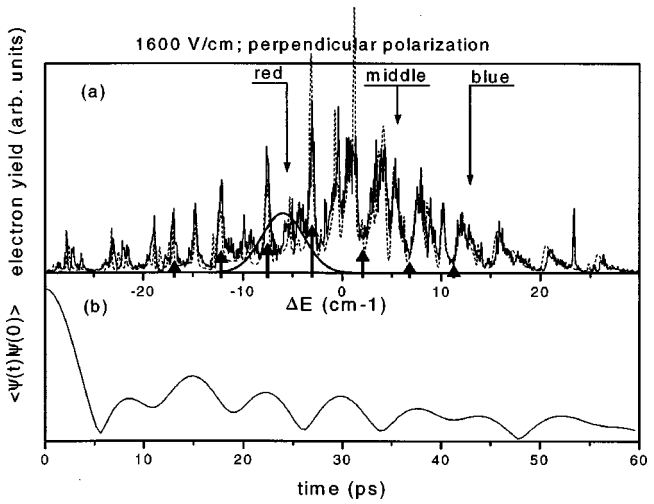

FIG. 2. (a) Ionization signal as a function of the detuning of the second narrow, band laser pulse. The barium atoms were excited with a polarization perpendicular to a static electric field of 1600 V/cm. The energy is with respect to the zero field position of the $5d7d$ state (41 841.66 cm^{-1}). The markers red, middle, and blue will be used as a reference in Figs. 3 and 5. The fat vertical arrows denote the position of the seven bluest Stark states of $n=22$, showing window resonances on the blue side of the perturber, where the arrows line up with valleys in the experimental spectrum. The sharp resonance at ~ 23 cm^{-1} is due to a slight (0.1%) strontium contamination of the barium sample. Note the excellent match with theory (dotted line). (b) Fourier transform of a convoluted spectrum with a width of 5.0 cm^{-1} and a detuning of -6.0 cm^{-1} (denoted by the Guassian curve in the upper graph).

the core, we populated a doubly excited state in barium by means of two narrow-band pulsed dye lasers in a static electric field. The first pulse, with a central wavelength of 413.4 nm and polarization parallel to the electric-field, excited ground-state electrons in barium to a $5d6p$ intermediate state; the $5d7d$ perturber region was excited by a second nanosecond pulse with a central wavelength near 567 nm and a bandwidth of <0.1 cm^{-1}. The polarization of this pulse was either chosen to be parallel or perpendicular to the electric field. An atomic barium beam was produced by a resistively heated oven. The barium atoms were excited between two parallel capacitor plates 10.0 mm apart. The electrons, created by the autoionization process, are pushed through the grid in the anode plate towards a set of multichannel plates. By scanning the second laser over the $5d7d$ perturber at a certain field strength we obtained the electron yield as a function of the detuning from the perturber. Great care is taken not to saturate the spectra with too much power; typically the power of the second laser was kept below 5 MW/cm^2.

In Fig. 2 (top) a typical absorption spectrum is depicted. The sharp features are the resonances arising from the Stark states in the $6s\epsilon k$ channels, while the overall broad feature is due to the coupling between the $6s$ channels and the $5d7d$ perturber and can be described by a Fano profile [9] with an asymmetry parameter (q) of -25. The width of this broad feature (≈ 15 cm^{-1} full width at half maximum) is representing the coupling strength between the perturber and the Rydberg series. The positions of the different resonances from the $6s\epsilon k$ channels can be related to positions of the very blue Stark states [3] of lower-lying n manifolds (as low as $n=22$, for 1600 V/cm). The reason that we are only seeing the blue states is because the wave function of these states is localized far from the saddle point; hence these states are long lived as opposed to red states, which ionize instantaneously. A further investigation of Fig. 2 also shows that the resonances in the $6s$ channels appear as dips (window resonances) on the blue side ($\Delta E>0$) of the perturber and as peaks on the red side of the perturber. This is due to the interference between electron waves from the different channels in the continuum channel. A theoretical calculation is depicted and the theory is in excellent agreement with experiment. To connect this absorption spectroscopy experiment to the Rydberg electron dynamics, we multiply an absorption spectrum with a Gaussian with a width and a central frequency corresponding to the width of a short broadband laser pulse. The Fourier transform of the achieved spectrum shows the recurrence spectrum in which we can see Stark beats due to the coherent superposition of the $6s\epsilon k$ Stark states. In Fig. 2 (bottom) a Fourier transform is depicted for a Gaussian pulse with a central wavelength of 566.77 nm and a pulse duration of 7.5 ps. Clearly, a beating pattern is resolved that is inversely proportional to the energy separation of the different Stark states (in atomic units): $\tau=2\pi/\Delta E$.

In order to measure the electron emission of the forced autoionization process, we have used an atomic streak camera [10] with picosecond resolution. The principle is as follows. Barium atoms are excited in a crossed-beam arrangement between two plates (separation=10.0 mm) over which the static field is applied. The second plate has a slit parallel to the beam direction through which the electrons can leave the interaction region. After this plate, a sweeping electric field is created (synchronized with the laser pulse) between two deflection plates, perpendicular to the previous plate set and perpendicular to the direction of the electron flux. This electric field typically sweeps from -0.5 kV to $+0.5$ kV in 500 ps. Therefore, electrons arriving at different times in the deflection region experience a different voltage and are recorded on a different position on a set of multichannel plates in combination with a phosphor screen that images the deflected electrons.

This experiment involved the investigation of the same doubly excited bound state, with the same excitation scheme as in the absorption spectroscopy experiment, except that the second narrow-band pulse is replaced by a picosecond pulse with a tunable central frequency. The recorded autocorrelation width of the amplified pulses (500 μJ, 10 Hz) of 10 ± 1 ps corresponding to a pulse duration of 7 ± 0.7 ps indicates that the pulses are near transform limited given the spectral width of 5 ± 1 cm^{-1}.

The streak camera experiment in its turn reveals information on when the wave packet is far from the core and the atom emits electron flux. In Fig. 3 three different electron emission traces (dots) are depicted at the same field strength (1600 V/cm), but for different values of the central wavelength of the ionizing broadband pulse. Note that the electron emission is not instantaneous, which could be expected due to the relatively strong coupling between the perturber and the structured continuum (0.8 ps). Instead, Stark beatings are resolved especially to the red side of the perturber. It appears that the ionization dynamics strongly depends on which wing

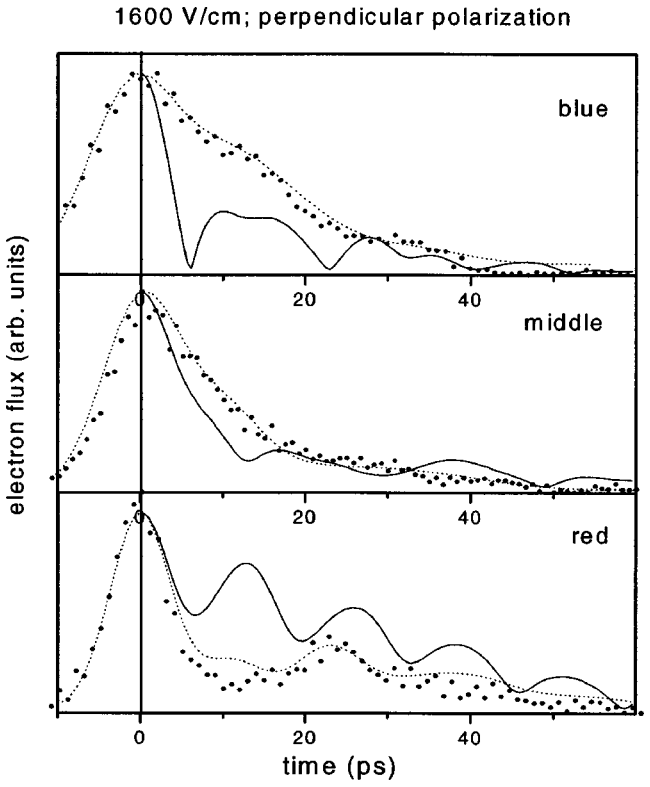

FIG. 3. Three electron emission traces (filled circles) taken with a 7.1-ps pulse at positions in the frequency domain corresponding with the labels in Fig. 2. Red has a detuning of $-11.0\ \mathrm{cm}^{-1}$, middle a detuning of $1.2\ \mathrm{cm}^{-1}$, and blue a detuning of $10.0\ \mathrm{cm}^{-1}$ with respect to the perturber. Each trace is compared to theory (dotted). Also Fourier transforms are depicted (solid lines) at the corresponding positions in the frequency domain.

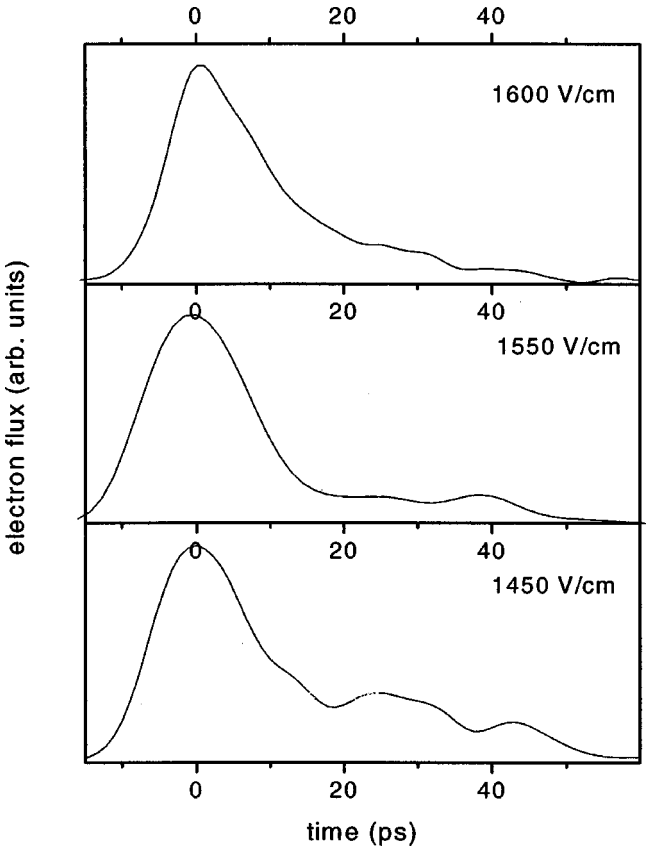

FIG. 4. Three electron emission traces with zero detuning but taken with different electric-field strengths, for perpendicular polarization.

of the perturber one is exciting: recurrences are strongest when one is detuned from the perturber and the overall structure is strongly influenced by the central wavelength of the ionizing pulse. At the center of the perturber there seems to be no effect of angular recurrences and the streak trace seems to follow a monotonic decay. At these three frequency positions we have performed Fourier transformations from the spectroscopy data in Fig. 2, and the results are depicted in Fig. 3 (solid line). The stronger recurrences on the red side of the perturber are due to the sharp resonances compared to the window resonances on the blue side. This effect can also be seen in the Fourier transform spectra. We have now probed the wave function of a two-electron system both near the core and when it is near the saddle point and able to autoionize due to the field. Note that the recurrence lifetime is not the same as the lifetime deduced from electron emission. This is particularly clear at the blue side, where the optical pump-probe experiment suggests that the lifetime is much shorter than the streak traces show. In fact, these measurements show that the electron is still bound (signal still to come in the electron emission) but not near the core (no more signal in the recurrence spectrum). We also studied the effect of changing the saddle-point position. Because strong electric fields are used, the saddle point is far away from the relevant $6s\epsilon k$ states in energy, and the detuning of the laser that excites to the $5d7d$ perturber has a negligible effect on the position in energy of the created wave packet above the saddle point. Therefore one can investigate the effect of the static electric field (that is, the position of the saddle point) and the detuning independently. The field at which the $n \sim 26$ Stark states are at the saddle point is 960 V/cm, and one would expect that it will be harder for the wave packet to escape over the saddle point as the field decreases towards this value. In Fig. 4 this effect is indeed observed: the electron flux extends out to much later times when the perturber is excited in a field that brings the perturber closer to the saddle point. Also we observe that, even though we are exciting at the center of the perturber, recurrences are starting to appear at 1440 V/cm, while at higher field strengths the streak traces at this position show a monotonic decay.

This series of experiments was also supported by theory, and in Fig. 3 each streak trace (dotted) is compared with calculation (solid). Clearly we have shown how powerful the theory is in reproducing the data from the two experiments. The calculations are based on the multichannel Stark theory developed in Refs. [5,7]. This formulation uses the WKB treatment of the Stark problem developed by Harmin [4] to obtain the dipole matrix elements and the wave function far from the nucleus. With this information and the asymptotic form of the wave function, we calculate the time-dependent flux of electrons when the system is excited by a pulsed laser. Previous (nondynamical) theoretical investigations of non-alkali-metal atoms in external fields were described in Refs. [1,8].

The calculation proceeds in two stages. In the first stage, we obtain the zero-field dipole-matrix elements and K matri-

ces for Ba by slightly modifying the results from an *R*-matrix calculation in *LS* coupling [7]. The spin-orbit effects are incorporated by using an *LS* to *jQ* frame transformation for the dipole matrix elements and the *K* matrices and using the experimental threshold energies to obtain the zero-field Rydberg states at the correct energies. In the second stage, the wave functions in spherical coordinates are transformed into parabolic coordinates [4] to account for the effects from the electric field in a nonperturbative manner. The time-dependent flux of electrons into the streak camera is simulated by superposing the energy-dependent wave functions with the appropriate coefficients that are the dipole-matrix elements and the energy-dependent amplitude for the photon [5]. In a previous investigation [1] of the same system a simpler model gave quantitative agreement due to lower resolution and the application of higher field strengths, which induced rapid field-induced ionization.

With the help of this extended theory we are now able to probe the effect of mixing, which could not be retrieved from the experiments. We focused especially on the singlet-triplet mixing of the $6s\epsilon k$ channels. The two relevant channels are denoted as the $6snd\ ^1D_2$ and the $6snd\ ^3D_2$ channel. In Fig. 5 a surprising effect is shown. The two graphs show the calculations of the electron flux with either singlet or triplet character. It appears that, even when one initially excites the mainly singlet character (red position), nearly all of the electron flux coming out at later times is due to the mixing of singlet character into triplet, while the singlet character decays almost instantaneously. Apparently only the sharp resonances have a long enough lifetime to acquire substantial mixing. Therefore at the perturber, where the decay is relatively fast, the singlet-triplet mixing is strongly suppressed. The effect is the strongest to the red side of the perturber where in the frequency spectrum the sharpest resonances were seen.

In conclusion, we have measured the process of forced autoionization both in the time domain and in the frequency domain. Both experiments revealed complementary dynamical information, which could be interlinked by performing

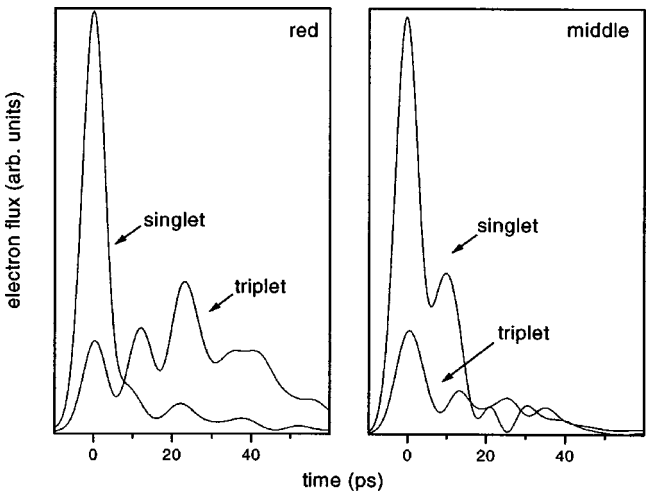

FIG. 5. The two panels show the calculated character of the electron flux at different energies (labels of Fig. 2). Clearly singlet-triplet mixing is observed, especially for the red case.

Fourier transformations. Stark beatings are observed in both experiments, even though we initially excite a deeply bound doubly excited state $(5d7d)$. Theoretical calculations yielded good agreement for both experiments. Therefore we were able to use theory as a third tool to study the dynamics involved in the forced autoionization process. In particular we focused on the effect of the singlet-triplet mixing. It appears that singlet character ionizes almost immediately, while the decay at later times has mainly a triplet character.

It is a pleasure to acknowledge the experimental assistance of D. I. Duncan in an early stage of this experiment. C.W. and L.D.N. were supported by the Stichting Fundamenteel Onderzoek van de Materie (FOM) and the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). F.R. was supported by the NSF. Computations were performed at the National Energy Research Supercomputer Center in Berkeley, CA.

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