Time-Gated Photoionization Spectroscopy Demonstrated for Cesium Rydberg Wave Packets in an Electric Field

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We introduce a new spectroscopic technique in which electron emission after optical excitation is measured with picosecond time resolution using a streak camera. By scanning the frequency of the exciting laser and measuring the electron flux in certain time gates, time-gated photoionization spectra are obtained. The technique is demonstrated for cesium Rydberg wave packets in an electric field of 1.0 kV/cm. The electron ejection probability is enhanced when the radial and angular oscillation periods of the excited wave packet are commensurable. [S0031-9007(97)04079-9]

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When an electron bound to a gas-phase atom, molecule, or even a surface is photoexcited by a short laser pulse above the ionization threshold, photoionization of the quantum system can occur. The time scale of photoelectron emission is known to be as short as a few picoseconds and depends on the excess energy of the photoelectron and hence the photon energy. Up to now the time scale of photoemission has been measured indirectly by spectroscopic techniques, essentially probing how long the electron resembles the initial conditions of the wave function directly after laser excitation. However, an electron not resembling the initial condition has not necessarily escaped. Hence the question what the delay of photoelectron emission is, as a function of photon energy, cannot be answered by conventional spectroscopy. In this Letter we introduce a new technique that measures directly the delay of photoelectron emission as a function of wavelength.

A conventional photoionization spectrum is obtained by measuring the time-integrated electron or ion yield as a function of the radiation wavelength [1]. Recurrences to the initial conditions, i.e., to the location of the electron just after optical excitation, are seen as peaks in the spectrum. For gas-phase atoms such recurrences are well described with closed orbit theory [2–4]. The width of these peaks is a measure of the number of recurrences the electron makes before escaping. Direct ejection of the electron only contributes to the background of the spectrum. Often, it is difficult to discriminate the background from the resonant peaks superimposed on it. This is especially true when the width of the resonance is comparable to the spacing between resonances; this situation occurs when the average number of recurrences ~1. Although conventional photoionization spectroscopy reveals recurrences [5], it does not disclose *when* the electron leaves the parent ion. For example, the electron could have a fixed probability for ejection during each recurrence or it could have a probability for ejection that changes drastically from one recurrence to the next. Using an atomic streak camera [6] we

record the time of electron emission after laser excitation. By setting time gates for the outgoing electron flux (see Fig. 1) and recording the yield in a time gate versus excitation wavelength we obtain a time-gated spectrum (TGS).

The inset of Fig. 1 demonstrates that TGS provides additional information on the electron dynamics that cannot be retrieved from conventional photoionization spectra or optical pump-probe studies. The inset shows both (1) the probability of the Rydberg electron recurrence to the cesium core in an electric field of 1.0 kV/cm, obtained by Fourier transforming the conventional ionization spectrum [7], and (2) the electron emission probability in the same
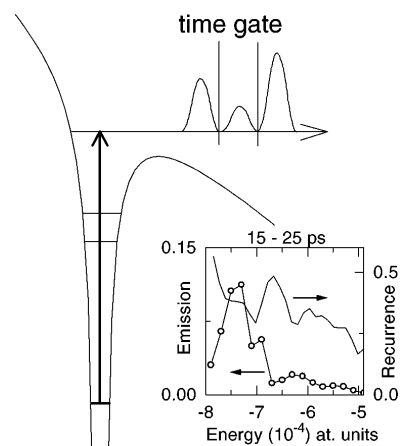

FIG. 1. Potential energy of an electron in a combined Coulomb and electric field ($V = -1/r - Fz$). The ionization of wave packets excited above the ionization threshold is measured in a time-resolved fashion using an atomic streak camera. The electron emission yield in a given time gate is measured as a function of the excitation energy, resulting in a time-gated photoionization spectrum (TGS) (dots in inset). Note the differences with the recurrences to the initial conditions $|\langle\Psi(0)|\Psi(\tau)\rangle|$ in the same time gate, as obtained by Fourier transforming the conventional spectrum of Cs. The laser excitation is perpendicular to the electric field of 1.0 kV/cm.

time interval [15-25] ps. While a detailed discussion on the interpretation of cesium time-gated spectra will follow in the remainder of this Letter, we would like to stress here that the time dependent flux into the atomic streak camera cannot be predicted from measurements of the energy dependent photoionization cross section (conventional spectroscopy); the cross section gives information about the sum of the absolute value squared of dipole matrix elements in all parabolic channels, whereas the flux depends on the size and relative phase of dipole matrix elements over an energy range.

In the TGS technique an atomic streak camera is used to measure the electron flux leaving the excited atoms (for a detailed description of the atomic streak camera see Ref. [6]). Atoms in a static field of typically 1 kV/cm are excited with a short optical pulse creating an autoionizing wave packet. The electrons leaving the atoms are accelerated by the field and enter a deflection region. By applying a fast electric pulse to one of the deflection plates the deflection angle of the electrons depends on the time of arrival between these plates; i.e., time is converted into a deflection angle. After a flight length the position of the electrons is measured using a position sensitive detector. The position of the electron determines the time the electron left the atom. By scanning the frequency of the exciting laser and recording the outgoing electron flux in certain time gates, time-gated photoionization spectra are obtained.

To excite the Rydberg wave packets a picosecond dye laser is used, which is pumped by the second harmonic of a mode-locked Nd:YAG (where YAG denotes yttrium aluminum garnet) laser operating at 76 MHz. The pulses are amplified using a three-stage dye cell amplification chain which is pumped by the second harmonic of a Nd:YAG laser operating at 10 Hz. The laser light (630–645 nm) is frequency doubled using a potassium dihydrogen phosphate crystal. The resulting pulses (~6 ps) are weakly focused in the interaction region ($I < 10^9$ W/cm^2). The static electric field (F) lowers the ionization threshold to $E_c = -2\sqrt{F}$ (atomic units are used, unless states otherwise). Autoionizing wave packets, located above the field-induced ionization threshold E_c are excited using a single-photon excitation step from the $6s$ ground state of Cs.

In Fig. 2 a photoelectron emission spectrum of an electronic wave packet, excited at $0.82E_c$ in an electric field of 1.0 kV/cm is shown. The time structure originates from the motion of the wave packet in the potential [8]. Because of the electric field the degeneracy of the angular momentum states is lifted, forming a Stark manifold of parabolic k states [9]. The bandwidth of the laser pulse is large enough to excite several k states coherently. Therefore, the angular momentum of the wave packet will oscillate with an oscillation period given by the inverse of the energy spacing between the excited k states [10]. Excited as a low angular momentum state, the wave packet begins to increase its angular momentum. After one angular precession period, the wave packet is back in low angular momentum states. At this time the Rydberg wave packet may scatter off the core [11,12] since the core electrons break the parabolic symmetry for the Rydberg electron. This scattering event can change the direction of the wave packet and cause it to travel down field giving rise to the observed peaks in the ionization spectrum. At 1.0 kV/cm and $E_c < E < 0$, k states belonging to different n manifolds overlap. Therefore, within the laser bandwidth, k states belonging to different n manifolds are excited.
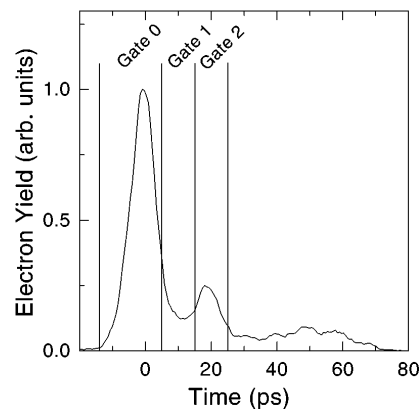

FIG. 2. Time-resolved ionization spectrum of a Cs Rydberg wave packet at $0.82E_c$. The polarization of the laser pulse (~6 ps) is chosen parallel to the electric field of 1.0 kV/cm. Also indicated are the time gates centered around multiples of the angular oscillation period of 10 ps.

To obtain a time-gated photoionization spectrum, time gates are set in a photoelectron emission spectrum such as shown in Fig. 2, and the relative yield in each gate is recorded while scanning the laser excitation wavelength. In Fig. 3 the relative ionization yields are measured for time gates centered around the prompt peak [Fig. 3(a)], the first [Fig. 3(b)], and the second [Fig. 3(c)] angular recurrence times of the wave packets [13]. The yield in each point is normalized to the total yield in the corresponding ionization spectrum. The laser polarization is chosen parallel to the electric field of 1.0 kV/cm. The background in the absorption spectrum corresponds to the yield in time gate 0 [Fig. 3(a)] since for those states the electron is ejected instantaneously on the time scale of the excitation pulse. Both the TGS gates around the angular recurrences show oscillations as a function of the excitation energy. Note that the oscillations have the same period but are out of phase with each other.

The calculations (full lines in Fig. 3) were performed in the manner described in Ref. [12]. The time dependent wave function is constructed by superposing the time independent wave functions with coefficients proportional to the dipole matrix element connecting the initial to the final states and to the spectral contents of the laser pulse. This calculation is somewhat more difficult than bound state wave packets since the final states are continuum states.
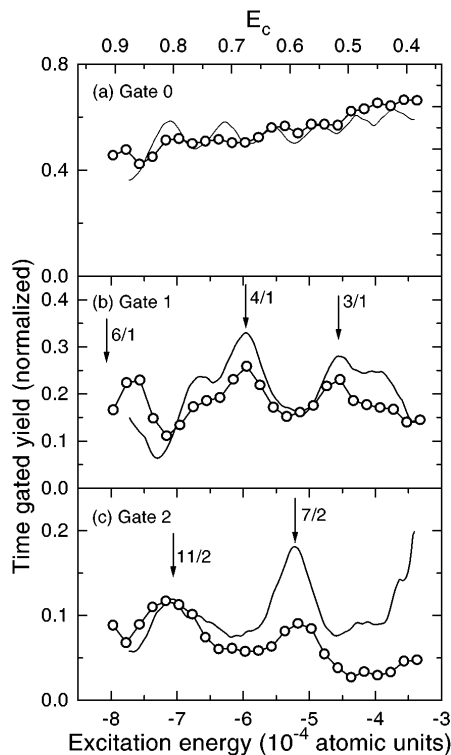
FIG. 3. Normalized TGS yield of Cs Rydberg wave packets in an electric field of 1.0 kV/cm as a function of the excitation energy. The yield is normalized to the total yield in the corresponding ionization spectrum. The measured (open circles) and calculated (full line) TGS spectra (a) for a time gate centered around the prompt ionization peak $(-\infty, 5 \text{ ps})$, (b) for a time gate centered around the first angular recurrence (5,15 ps), and (c) for a time gate centered around the second angular recurrence (15,25 ps). The arrows indicate the commensurability of the radial and angular periods of the electron dynamics (see text).

We construct the time independent wave function by performing a coupled channel calculation in parabolic coordinates [11]. The flux into the detector can be calculated by utilizing the asymptotic form of the atomic functions in parabolic coordinates. The coupling between the channels occurs through the scattering of the valence electron off the core as represented by nonzero quantum defects for each ℓ partial wave. For hydrogen, all of the quantum defects are zero, and there is no scattering between parabolic channels. For cesium, the s, p, and d waves contribute to the scattering.

The yield in time gate 0, corresponding to the background in a conventional spectrum is monotonically increasing with energy as can be expected since the solid angle in which an electron can directly escape is increasing with energy. The mechanism responsible for the small oscillations in time gate 0 of Fig. 3 arises from the fact that the laser pulse is long compared to the radial period. This means the electron wave that is excited during the first part of the laser pulse can interfere at the nucleus with the wave excited during the latter part of the pulse. The construc-

tive or destructive interference gives rise to the observed oscillations.

The underlying mechanism responsible for the oscillations observed in Figs. 3(b) and 3(c) can be explained in terms of the commensurability between angular and radial periods of the electron dynamics [14]. Within the laser bandwidth, k states belonging to different n manifolds are excited. While the angular recurrence time is given by the inverse of the energy spacing of adjacent k states within the same n manifold, the radial recurrence time is given by the inverse of the energy spacing between extreme k states from the n and $n + 1$ Stark manifolds.

The energies where the two periods commensurate are indicated by the 6/1, 4/1, and 3/1 arrows in Fig. 3(b), corresponding to an angular/radial oscillation time of 10.5/1.8, 9.2/2.3, and 8.6/2.8 ps, respectively. From Fig. 3(b) it can be seen that the TGS signal is larger at the first angular recurrence whenever the angular period is an integer multiple of the radial period. States around $n = 25$ are excited, meaning that the angular momentum will oscillate between $l = 0$ and $l = 24$. It is found [11] that the wave packet can only scatter down field when it is in the lowest angular momentum states, i.e., ns, np, and nd states. When the wave packet is not near the core in the radial coordinate at the time of low angular momentum, scattering to the ionizing red states will not take place, leading to a suppression of the ionization yield in time gate 1. This is observed in Fig. 3(b) where the TGS signal reduces when the two periods are out of phase at the first recurrence. When the radial and angular periods are out of phase at the first angular recurrence, they are in phase at the second angular recurrence. Therefore the oscillations in the TGS spectrum for the second angular recurrence [Fig. 3(c)] show maxima at these points given by 11/2 and 7/2. At the 5/1 point $(0.76E_c)$, determined by scaled energy spectroscopy [4], the time-gated yield of Fig. 3(b) only shows a small increase. Inspection of the hydrogenic energy levels shows that the absence of this peak in the spectrum is caused by a quantum effect: There are no blue states present at this field strength to satisfy the 5/1 commensurability. For the same reason the 9/2 maximum is missing in Fig. 3(c).

The ionization mechanism described here should not restrict itself to Cs. In Fig. 4 the calculated TGS spectra for the elements Cs, Rb, and Li are plotted. Again the time gates are centered around the first and second angular recurrences of the wave packet. The Rb and Cs spectra show great similarities, but for Li some deviations can be found in the TGS spectrum belonging to the second angular recurrence [see Fig. 4(b)]. Cs and Rb should be similar because their p- and d-wave quantum defects are near half integer and the s-wave reduced quantum defect is small but not negligible; Li only has an s-wave quantum defect substantially different from 0. At the 4/1 commensurability there also appears a peak in the TGS spectrum for the second angular recurrence (8/2). For Li
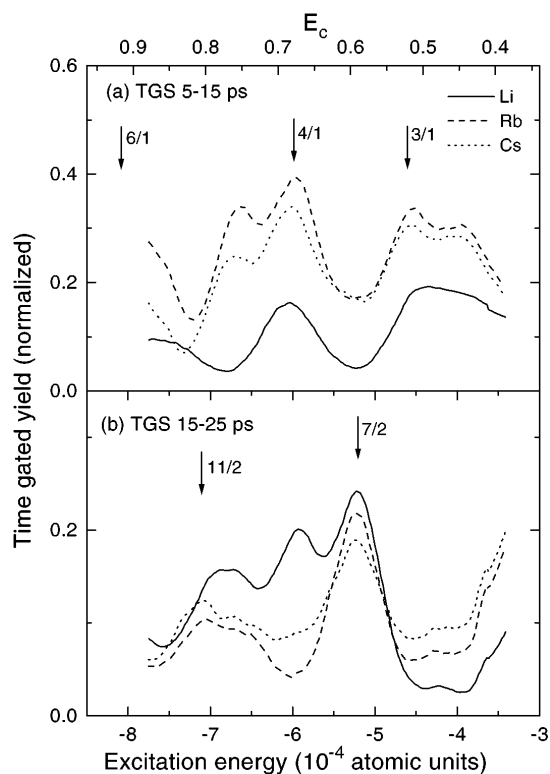
FIG. 4. Calculated normalized TGS spectra in a static electric field of 1.0 kV/cm for Li (full line), Rb (dashed line), and Cs (dotted line). (a) Shows the TGS spectra for a time gate centered around the first angular recurrence (5-15 ps) and (b) for a time gate centered around the second angular recurrence (15-25 ps).

the ionization occurs on a longer time scale than for Cs or Rb due to the much smaller quantum defects, which causes the scattering. Within our time dependent language, we say that the electron can return as s, p, or d waves in Rb and Cs and scatter down field, whereas the electron must return as an s wave to the small Li core in order to scatter down field. Therefore, even at the 4/1 point in the Li spectrum, the Rydberg population has not been depleted after the first angular recurrence. At the second angular recurrence both radial and angular motion are in phase again (8/2) giving rise to a relatively large yield at the second angular recurrence.

In conclusion, we have described a novel spectroscopic tool called time-gated photoionization spectroscopy. Information in both the frequency and time domain is obtained simultaneously with this technique. TGS provides additional information on the time of photoelectron emission compared to conventional absorption spectroscopy. We have experimentally demonstrated the technique on the

photoionization of Cs wave packets in a static electric field. It is found that the time-gated spectra reveal information on the commensurability between radial and angular oscillation periods of the excited wave packets. An enhancement in the ionization yield is found whenever the wave packet is in a low angular momentum state *and* has radially returned to the core, since core scattering is the relevant ionization mechanism. These calculations show furthermore that this mechanism, unraveled by the Cs experiment is also applicable to other atoms, such as Rb and Li.

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