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Atomic hydrogen in a strong optical radiation field

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Experimental energy spectra and energy-resolved angular distributions of photoelectrons produced by multiphoton ionization of atomic hydrogen are presented for several wavelengths between 596 and 630 nm, peak intensities of about 10^{14} W/cm², and laser pulse durations of about 0.5 ps. Resonant ionization processes via ac Stark-shift-induced resonances with excited states dominate the spectra. The results of Sturmian-Floquet calculations of these spectra and angular distributions are presented; they are in fair agreement with the experimental data.

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I. INTRODUCTION

In this paper, experimental energy spectra and energyresolved angular distributions of photoelectrons produced by multiphoton ionization of atomic hydrogen are presented in detail for several wavelengths between 596 nm and 630 nm, peak intensities of about 10^{14} W/cm², and laser pulse durations of about 0.5 ps. In addition, the results of a large scale calculation of these spectra and angular distributions in the Sturmian-Floquet method are reported. We discuss the importance of the different processes contributing to the energy spectra under these experimental conditions and investigate whether measurements of energy resolved photoelectron angular distributions can be used to characterize the bound excited states which give rise to resonance enhancements in the spectra.

Much progress has been made in understanding the interaction of atomic systems with strong laser fields through the experimental and theoretical investigation of multiphoton ionization (MPI) processes and high-order harmonic generation [1]. Three regimes can be identified for the interaction process, a long-, a medium-, and a short-wavelength regime. In the short-wavelength regime the phenomenon of *adiabatic* stabilization in a strong radiation field has stimulated much theoretical work [2], trying to reveal its physical reason and to find systems usable for experimental observation. Recent work by de Boer *et al.* gave a direct experimental hint on the effect [3].

In the long-wavelength limit, investigations into highorder harmonic generation [4] showed the close relationship between this process and tunnel ionization of atoms in this low-frequency regime [5].

In the medium- (visible) wavelength range, which will be discussed in this paper, a decisive step forward in understanding the high-intensity laser-atom interaction process was made with the experimental demonstration of the existence of resonance structures in the photoelectron kinetic energy spectra. They were first observed in MPI of xenon by subpicosecond laser pulses by Freeman and co-workers [6]. Similar structures were subsequently found in MPI of helium [7] and atomic hydrogen [8]. These experiments revealed the important role resonance enhancement plays in photoionization of atoms in a strong optical (medium wavelength) radiation field.

Resonances are induced by large ac Stark shifts, when the atomic ground state and some excited states are shifted into multiphoton resonance at certain intensities during the passage of the laser pulse [6–8]. This may be understood easily with the help of Fig. 1. Classically, a highly excited electron nearly moves as a free particle along most of its Kepler orbit; the external electric field induces an oscillation about its unperturbed trajectory, with the same angular frequency ω as the laser radiation. Its cycle-averaged energy therefore increases by a quantity P, the ponderomotive energy. That is the mean kinetic energy of the quiver motion of a free electron in the field. P is inversely proportional to the square of the frequency and directly proportional to the intensity $I: P = 2\pi e^2 I/mc\omega^2$, where e and m are the charge and

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FIG. 1. Schematic energy level diagram of atomic hydrogen, showing the shift of the ground state (which is equal to the ponderomotive energy, since we keep the threshold energy fixed at E = 0) as a function of radiation intensity. The excited states with principal quantum number $n \ge 4$ do not move much with varying field intensity, while the n = 2 and n = 3 states move significantly (their energy levels are not drawn beyond 10^{13} W/cm²). The arrows indicate an ionization process at 608 nm at a specific intensity. The dashed lines represent the ground state with $N = 5, \ldots, 9$ photons added.

mass of the electron. At 608 nm, $P = 3.452 \times 10^{-14} I$ when P is expressed in eV and I in W/cm^2 . P has been subtracted from the energy of all states represented in Fig. 1 for the sake of comparison with theoretical results in Sec. III. We thus keep the threshold fixed at E = 0. The resonance intensities for different excited states of xenon, and therefore their ac Stark shifts, have been investigated by Agostini and co-workers as functions of the wavelength of the incident laser [9]. They observed that the energy shift of excited states is indeed close to P, independent of the specific state. In contrast, the ground state of the atom is much less perturbed by the laser field than the Rydberg states, and the laser-induced shift of its energy is smaller. In good approximation, it is about P/20 near 600 nm wavelength and intensities of the order of 10^{13} W/cm². Thus a photoelectron ejected at intensity I leaves the atom with a drift kinetic energy E_{kin} , which depends on I through the equation

$$E_{kin}(I) = E_{1s}(I) + N\hbar\omega$$

$$\approx E_{1s}(0) - P + N\hbar\omega, \qquad (1)$$

where $|E_{1s}(I)|$ is the ionization potential of the ground state in the presence of the laser field. The strong dependence of the ionization potential on intensity results in a dependence of the minimum number $N_0(I)$ of photons necessary to ionize the atom on intensity. If one writes the total number N of photons absorbed as the minimum mumber $N_0(I)$ necessary for ionization plus the number S of photons absorbed "in the continuum," the kinetic energy of the photoelectrons is

$$E_{\rm kin}^{S}(I) = E_{1s}(I) + [N_0(I) + S]\hbar\omega.$$
 (2)

Ponderomotive scattering, i.e., the acceleration experienced by an electron traveling through an inhomogeneous laser field, usually modifies the kinetic energy of the photoelectrons and their angular distribution if the laser pulse duration exceeds 1 ps, for a focused beam. This has been investigated in great detail both experimentally and theoretically [10]. If the pulse duration is less than a picosecond, photoelectrons with a moderate kinetic energy do not move significantly through the focused laser beam during the passage of the pulse. In this case, ponderomotive scattering can be neglected and the photoelectrons retain the velocity they have when they are created inside the beam. The use of laser pulses short enough for ponderomotive acceleration to be insignificant was an essential feature of the experiments which established the importance of Stark-shift-induced resonances in strong-field multiphoton ionization.

For our experimental conditions, namely, laser pulse durations of about 0.5 ps and a focal spot size of about 15 μ m, we are in the short-pulse regime for MPI. Photoelectrons with kinetic energies of a few eV do not move appreciably in the laser focus during the pulse. Their kinetic energy is thus changed only slightly by ponderomotive acceleration. We therefore measure the kinetic energy $E_{\rm kin}^S(I)$ which the photoelectrons have in the laser beam when they are released from the atom [6,8,11]. Typically, the spectrum would consist of groups of narrow peaks repeated at energy intervals $\hbar\omega$, corresponding to photoelectrons preferentially ejected at intensities where the ionization process is enhanced by a Stark-shift-induced intermediate-state resonance.

The remaining ponderomotive acceleration in the short pulse will lead to a broadening of structures in the photoelectron spectrum. Under our experimental conditions, i.e., pulse duration, focal spot size, and pulse peak intensity, one estimates a broadening of less than 60 meV through ponderomotive acceleration at an electron kinetic energy of 1 eV. With increasing initial kinetic energy the broadening increases in proportion to the square root of $E_{kin}^{S}(I)$.

Studying MPI in atomic hydrogen instead of rare gases makes it possible to carry out a *detailed* comparison between experimental data and the results of calculations that do not involve approximations to the structure of the atom in a significant way. A large amount of work has now been devoted to the theoretical study of the interaction of atomic hydrogen with strong electromagnetic radiation. In particular, ionization rates and/or angular distributions of the ejected electrons have been calculated by direct numerical integration of the timedependent Schrödinger equation for very short incident laser pulses consisting of only a few optical cycles [12], by reducing the problem to a time-independent one using the Floquet approach for long pulses [13-16] or by using methods based on the extrapolation of perturbation series [17,18]. For the present physical situation a direct solution of the time-dependent Schrödinger equation does not yet appear feasible, since the pulses are too long (several hundred cycles of the field). For a slowly varying laser pulse envelope, the Floquet results yield accurate fully differential intensity-dependent data, which may subsequently be integrated over the experimental pulse parameters.

In the following section we present the experimental setup, defining all parameters that have to be taken into account in the theoretical modeling. Section III briefly describes the Floquet method and the subsequent folding of the intensity-dependent results with the laser pulse in order to obtain the same differential information as measured experimentally. In Sec. IV we discuss the results (kinetic-energy spectra and angular distributions) in detail, both the experimental and theoretical ones. Finally, conclusions and an outlook are presented.

II. EXPERIMENT

The MPI experiment is done by using a high-power subpicosecond laser system. The laser oscillator consists of a hybrid mode-locked dye laser, synchronously pumped by the second harmonic of an active mode-locked Nd:YAG laser (where YAG denotes yttrium aluminum garnet) at a pulse repetition rate of 76 MHz. The dye laser is operated in the wavelength range from 590 nm to 630 nm with the dyes Rhodamine 6G and Rhodamine B in the short- and long-wavelength ranges, respectively. Also depending on the wavelength we use other organic dyes as saturable absorbers.¹ The dye laser delivers pulses with an energy of 2 nJ and a pulsewidth [full width at half maximum (FWHM)] in the range from 0.3 ps to 0.5 ps, depending on wavelength.

These pulses are amplified in a four-stage dye amplification chain, pumped by the second harmonic of a Q-switched Nd:YAG laser at a repetition rate of 10 Hz. The final pulse energy is 0.5 mJ. To suppress amplified spontanous emission the first, second, and third amplifiers are decoupled from each another by pinholes and saturable absorbers. The remaining amplified spontaneous emission amounts to about 1-2% of the final pulse energy. Since it is spread over about 5 ns, its intensity is negligible.

The width of the amplified pulses is again 0.3-0.5 ps. Single-shot second-order autocorrelation traces of the pulses can be fitted quite well with the assumption of a sech² pulse shape with deviations in the wings of the pulse. The autocorrelation measurement does not allow the reconstruction of the pulse shape. The autocorrelation traces reveal pulse to pulse fluctuations of the pulsewidth (and therefore of the peak intensity), with a standard deviation of roughly 20% of the mean pulsewidth. The fluctuations in pulse energy are much smaller and have a standard deviation of roughly 2%.

The amplified laser beam is focused onto the atomic hydrogen target, as depicted in Fig. 2, using a lens with



FIG. 2. Schematic diagram of the experimental setup and the geometry of the interaction and detection arrangement (not to scale).

100 mm focal length and an aperture selecting only the central spot of the far field beam pattern. The resulting focal spot is smooth, with a diameter (FWHM) of about 15 μ m. The peak intensity reaches 10^{14} W/cm². A half-wave plate in combination with a polarizer is used to attenuate the laser beam and fix the direction of linear polarization. A second half-wave plate serves to rotate the light polarization with respect to the direction of detection of photoelectrons.

Atomic hydrogen is generated in a microwave discharge in molecular hydrogen at a pressure of about 1 mbar [19]. To achieve efficient dissociation a continuous flow of H_2 through the discharge is maintained. A small fraction of this flow is passed through a capillary into the interaction region with the laser beam in the main vacuum chamber. The capillary (aperture ~ 0.5 mm) forms an effusive atomic beam. The gas density over the whole focal volume can be taken as constant. The base pressure in the main vacuum chamber is less than 10^{-7} mbar and rises to about 4×10^{-6} mbar with the introduction of atomic hydrogen. We estimate the dissociation of $H_2 \rightarrow 2H$ to be only about 50% effective and therefore expect a background from multiphoton ionization of H_2 . Two facts are responsible for photoionization of H_2 not masking the ionization signal from atomic hydrogen. First, the ionization probability of H_2 is small compared with the atomic one under our experimental conditions. Second, the molecular photoelectron spectrum is broad and structureless.

Photoelectrons from the MPI process are detected perpendicular with respect to the laser beam and the effusive atomic beam after passage through a time of flight energy analyzer [8,19,20]. The detector itself consists of a circular double channel plate. The target density is adjusted so that space charge effects are negligible. Then the total number of electrons recorded per laser shot is only 1–2.

Some small contact potentials are present along the drift path of the electrons. Transforming the photoelectron spectra from time of flight to kinetic energy, we assume the contact potential to be homogeneous and localized over a small part of the drift path (the region

¹Namely, 3,3'-diethyloxadicarbocyanine-iodide (DODCI), 1,3'-diethyl-4,2'-quinolyloxacarbocyanine-iodide (DQOCI), or 1,3'-diethyl-4,2'-quinolylthiacarbocyanine-iodide (DQTCI).

between the exit slit and the entrance of the drift tube; see Fig. 2). The focal region is known to be potential-free. At an electron kinetic energy of 1.8 eV the spectrometer provides an energy resolution of about 60 meV, which changes with the energy E in proportion to $E^{3/2}$. The energy analyzer is calibrated by taking time of flight spectra of photoelectrons from MPI of xenon or of atomic hydrogen with the second harmonic ($\lambda = 532$ nm) of a Q-switched Nd:YAG laser, which delivers pulses of ~ 6 ns pulsewidth. Under these conditions the kinetic energy of the ATI photoelectron groups is known from previous experiments [19,21–23].

In addition to energy analysis the spectrometer allows the measurement of energy-resolved angular distributions of the photoelectrons. Angular distributions are recorded by turning the polarization of the laser beam with respect to the direction of detection of the photoelectrons in steps of 9°. The angular resolution of the instrument as determined by the angle subtended by the detector is 5° , corresponding to a solid angle of 0.024 sr.

The output of the double-channel-plate detector is amplified and fed into a transient recorder (sampling rate 500 MHz, 1024 channels). Time of flight spectra are accumulated in a computer for a preselected number of laser pulses.

III. THEORY

A. Floquet theory of MPI

The theory has been reviewed recently [24] and here we only sketch it for completeness. We assume that the radiation field is nearly monochromatic (chirping is neglected), so that the (classical) vector potential is $\mathbf{A}(t) = \mathbf{A}_0 \sin \omega t$, where the amplitude \mathbf{A}_0 and therefore the intensity $I \equiv \omega^2 |\mathbf{A}_0|^2 / (8\pi c)$ are slowly varying in time on the scale of one cycle $2\pi/\omega$. Making the dipole approximation, working in the velocity ($\mathbf{p} \cdot \mathbf{A}$) gauge, and transforming out of the Hamiltonian the term in \mathbf{A}^2 , the interaction V(t) of the atom with the radiation can be expressed as

$$V(t) = V_+ e^{-i\omega t} + V_- e^{i\omega t}, \qquad (3)$$

where the operators V_+ and V_- vary only slowly with time. Taking advantage of the near periodicity of V(t), we remove a dynamical phase factor $\exp\left(-i\int^t dt' E/\hbar\right)$ from the state vector $|\Psi(t)\rangle$ and express the residual fac-

from the state vector $|\Psi(t)\rangle$ and express the residual factor in a harmonic series:

$$|\Psi(t)\rangle = \exp\left(-i\int^{t}dt' E/\hbar\right)\sum_{n=-\infty}^{\infty}e^{-in\omega t}|\psi_{n}\rangle.$$
 (4)

We now adopt the Floquet ansatz, which amounts to neglecting altogether the slow temporal variation of the harmonic components $|\psi_n\rangle$. The time-dependent problem can thereby be reduced to a time-independent one; substituting the Floquet ansatz into the time-dependent Schrödinger equation gives the eigensystem of coupled equations,

$$(E + n\hbar\omega - H_a)|\psi_n\rangle = V_+|\psi_{n-1}\rangle + V_-|\psi_{n+1}\rangle, \quad (5)$$

where H_a denotes the Hamiltonian of the field free atom. Solving this system subject to outgoing-wave boundary conditions yields the (complex) quasienergy E. The rate of ionization from the dressed state whose quasienergy is E can then be calculated at each instantaneous value of the intensity. The total rate of ionization, integrated over all angles of emission and summed over all channels (a channel being labeled by the net number N of photons absorbed), is $\Gamma = -2 \text{ Im} E/\hbar$. The differential rate for the electron to absorb N photons and be ejected with velocity \boldsymbol{v}_N is $\boldsymbol{v}_N |f_N(\boldsymbol{v}_N)|^2$, with $\mu v_N^2/2 = \text{Re}E + N\hbar\omega$. The ionization amplitude $f_N(\boldsymbol{v}_N)$ can be written in various (equivalent) forms; the form that we used in our calculations is [13]

$$f_N(\boldsymbol{v}_N) = -\sqrt{2\pi} \frac{\mu}{\hbar^2} \sum_n J_{n-N}(\rho_N) \langle \Phi_{\boldsymbol{v}_N}^- | H_a^\dagger - H_a | \psi_n \rangle.$$
(6)

In this equation, $\rho_N = -(e/c\hbar\omega)\boldsymbol{v}_N\cdot\boldsymbol{A}_0$ and $|\Phi_{\boldsymbol{v}_N}\rangle$ is the scattering vector of an unbound electron emerging with velocity \boldsymbol{v}_N from the Coulomb field of the nucleus in the absence of radiation, normalized according to $\langle \Phi_{\boldsymbol{v}}^-|\Phi_{\boldsymbol{v}'}^-\rangle = \delta(\boldsymbol{k}-\boldsymbol{k}')$, with $\boldsymbol{k} = \mu \boldsymbol{v}/\hbar$. The normalization of the ionizing Floquet state must be calculated as $\sum_n \langle \bar{\psi}_n | \psi_n \rangle = \sum_n (\psi_n | \psi_n) = 1$, where $\langle \bar{\psi} |$ denotes the adjoint state vector and thus the scalar product (a|b)involves no complex conjugation.

We should stress that Eq. (6) gives the amplitude for N-photon ionization from a single Floquet state. Near a resonance, where two Floquet states participate, Eq. (6) is not correct. Rather, near a resonance, the atom must be described by a linear combination of two Floquet states whose time-dependent coefficients (which depend on the pulse shape) may be obtained by substituting the linear combination into the time-dependent Schrödinger equation. However, we have not implemented this coupling of two Floquet states; instead we have simplified matters by describing ionization as proceeding from a single Floquet state even on resonance. This simplification does not invalidate our estimates of the positions and widths of the resonances, but it does call into question our estimates of branching ratios (i.e., of relative heights of resonance peaks in the photoelectron energy distribution) as well as our estimates of angular distributions.

Figure 3 gives the energy level positions of the ground and some excited states of hydrogen at the wavelengths 616 and 596 nm. We see that some of the main features of the simple model of Fig. 1 are confirmed, as shall be discussed in Sec. IV. A below. However, strong couplings between excited states are also visible, which give rise to many crossings and avoided crossings as a function of field intensity.

At intensities near a resonance, the quasienergy is nearly degenerate (modulo $\hbar \omega$). As a resonance is passed, the real parts of the two nearly degenerate quasienergies undergo a true or avoided crossing. If the crossing is avoided, the atomic characters of each of the adiabatically evolving Floquet eigenstates switch as the resonance



FIG. 3. Real part of the Floquet quasienergies for the ground and several excited states in a linearly polarized laser field of wavelength 596 nm (left) and 616 nm (right) versus field intensity. The energies have been shifted by the appropriate multiple of the photon energy to exhibit the resonance crossings with the (1s) ground state.

is passed. If the gap at the avoided crossing is very small (the gap is about equal to the Rabi coupling energy) and the intensity varies sufficiently rapidly so that the time of passage through the resonance is small compared to the Rabi flopping time, then the atom will stay on the diabatic curve. In the case of atomic hydrogen, the gaps at avoided crossings between the real parts of the 1s quasienergy and other quasienergies are usually very narrow at wavelengths in the visible (for example, all the gaps are smaller than 0.0002 a.u. at 616 nm and intensities below 1.2×10^{14} W/cm²), and the diabatic 1s state is clearly defined. At a true crossing the ionization width of the upper (Rydberg) level is usually larger than the Rabi energy and the ionization width of the lower (initial) state is more or less the rate for excitation of the upper state; once the upper state is excited, it decays rapidly on the time scale set by the inverse Rabi frequency.

Figure 4 shows the total ionization rates for the four wavelengths considered in the spectra below. The markers pinpoint a few intensities (given in 10^{13} W/cm²). The shift of the real part of the 1s energy is indicated in abscissa, with zero taken as the energy where the seven-photon ionization threshold is crossed (downwards). Thus all seven-photon resonances appear at the same positions, showing that for all wavelengths the resonances are similar, but appear at quite different intensities: the concomitant ionization rates also differ strongly.

In order to explore in more detail the dominant feature of the spectra, namely, the 4f resonance, Fig. 5 shows the trajectories of the 1s and 4f states in the complex energy plane, at a wavelength of 616 nm. We observe a true crossing in the real part at an intensity of approx-



FIG. 4. Imaginary part of the Floquet quasienergy for the ground state of hydrogen in a linearly polarized laser field at 596, 608, 620, and 630 nm, respectively, versus the shift of the ground state plus $7\hbar\omega$, so that the energy where the threshold for seven-photon ionization is crossed is 0 (the thin vertical line). The markers denote three specific field intensities, indicated in units of 10^{13} W/cm².

imately 3.65×10^{13} W/cm². The width of the 4f state is very large, and it is practically not perturbed by the 1s state. 1s, on the other hand, has a very small width (the imaginary part has been multiplied by a factor 1000 in the figure), and this width is significantly enhanced by the seven-photon resonance with 4f. In order to describe this crossing in a time-dependent formulation, Landau-Zener theory in a simple form cannot be used since it is only formulated for avoided crossings. A proper timedependent calculation must take the widths into account also.

We should note that the resonance occurs at an intensity for which the width of the 4f state begins to decrease with increasing intensity. (This is also the case at 596 nm.) The decrease may simply be the falling



FIG. 5. Trajectories in the complex energy plane of the Floquet quasienergies of the 1s and 4f states in a linearly polarized field of wavelength 616 nm. E_{4f} has been shifted by -7ω . The markers denote three different intensities, given in units of 10^{13} W/cm². The true crossing of the real parts occurs close to an intensity of 3.65×10^{13} W/cm². The scale for the imaginary part of the 1s pole has been expanded by a factor of 1000.

edge of a resonance enhancement, associated with the avoided-crossing-like variation of the real part of the 4f quasienergy visible in Fig. 3 at about 3×10^{13} W/cm². The decrease may also manifest the onset of adiabatic stabilization of this state. Although the 1s-4f crossing occurs at different intensities for different frequencies, the variation with frequency of the 4f peak in the 1s rate is not very pronounced (see Fig. 4); owing to the limited resolution, the decrease in width of the 4f state is therefore not clearly visible in the experimental data.

Numerical calculations were performed on a discrete basis set composed of radial complex Sturmian functions and spherical harmonics. The total ionization rate was computed over a fine mesh of intensities. Since computation of *differential* rates is much more demanding, we limited ourselves to interpolating a sample of angular distributions calculated at 50 or so different intensities. In the range of intensities giving the dominant contribution to the spectra, up to about 7×10^{13} W/cm², the partial rates (i.e., the differential rates integrated over all emission angles) for ejection into the lowest five open channels summed to about 90-100% of the total rate; that they did not sum to exactly 100% can be attributed to the contribution of the omitted channels, whose relative importance grows with intensity and to numerical inaccuracies in the angular distributions for ten- (or more) photon ionization. Due to these inaccuracies, the theoretical results are not reliable for photoelectron energies larger than 6 eV.

Figure 6 illustrates these differential data: in Fig. 6(a)we show the branching ratios, which are the ratios of the partial rates to the total rate (minus twice the imaginary part of the quasienergy), versus intensity, for emission into the lowest three ATI channels, integrated over all angles. Figure 6(b) shows the same branching ratios, but including angle-differential information: only the part within a cone with a 5° aperture about the polarization axis is counted. The general resonance features are the same in Figs. 6(a) and 6(b), with a few notable exceptions, depending on the photon channel (e.g., the 2s peak in the N=9 channel, the 4p peak in the N=9channel, or the 4f peak in the N=10 channel) and with significant differences in the relative heights of many resonance peaks. This may surprise, since as a function of the direction of ejection (θ, ϕ) , the ionization rate is sharply peaked about the direction of the polarization vector ($\theta = 0$). However, ejection outside a 5° cone centered about this direction contributes significantly to the total photoelectron yield, owing to the $\sin \theta$ factor weighting the probability that a photoelectron be ejected at an angle θ . Since the angular distribution varies from resonance to resonance and from above-threshold ionization (ATI) channel to ATI channel, the yield in electrons ejected within the cone is not quite proportional to the yield integrated over ejection angle. It is thus important to take the angular distribution of the electrons into account when comparing theory to experiment.

B. Steps in modeling the experiment

In order to take into account spatiotemporal effects, we integrated the differential rate for ionization from the



instantaneous 1s diabatic state over space and time to give the yield in photoelectrons, allowing for the gradual disappearance of target atoms due to photoionization. The intensity profile adopted in the calculations is that of a Gaussian beam with a sech² temporal envelope:

$$I(\rho, z, t) = [R^2/r^2(z)] I_0 e^{-2\rho^2/r^2(z)} \operatorname{sech}^2[(t - z/c)/\tau],$$
(7)

with $r^2(z) = R^2[1 + (2zc/\omega R^2)^2]$. The yield scales with the spot size at the laser focus R as R^3 , provided, as we assumed, that the target is initially homogeneous in the vicinity of the focus. Using alternatively a gaussian profile in time instead of a sech² profile did not modify the energy spectra in any significant way. In the calculations $R = 12.7 \ \mu m$ is used. This corresponds to a FWHM of the beam at the waist of 15 μm . The pulse duration is the average FWHM of the pulse, $\Delta t_{\rm FWHM}$. Accordingly, in the equation above $\tau = \Delta t_{\rm FWHM}/(2 \cosh^{-1}\sqrt{2}) = \Delta t_{\rm FWHM}/1.763$.

The pulse duration $\Delta t_{\rm FWHM}$ and peak intensity I_0 are either fixed to their average values [e.g., $\Delta t_{\rm FWHM} = 0.5$ ps and $I_0 = 6.6 \times 10^{13}$ W/cm² in the case of an experiment performed with pulse peak intensity and pulse width of $(6.6 \pm 1) \times 10^{13}$ W/cm² and 0.5 ps] or are al-



lowed to fluctuate from pulse to pulse as follows. The experimental average peak intensity $\langle I_0 \rangle$ and average pulse duration $\langle \Delta t_{\rm FWHM} \rangle$ are used to define an average pulse energy $\langle E \rangle = \langle I_0 \rangle \times \langle \Delta t_{\rm FWHM} \rangle$. Then the energy and duration of each pulse are selected at random, assuming that they vary independently from each other with probability distributions that are Gaussian with means $\langle E \rangle$ and $\langle \Delta t_{\rm FWHM} \rangle$, respectively, and standard deviations that are 2% of the mean for the energy and 20% of the mean for the duration are then converted into intensity. Pulses with I_0 larger than a preset maximum intensity are discarded.

The yield of photoelectrons along the direction of the polarization of the light is further averaged over angle and energy in order to model the finite resolution of the detector used in the experiments. We have performed a multitrajectory Monte Carlo calculation in order to model the fluctuating parameters of the experiment, including the ponderomotive acceleration which the photoelectrons undergo on their way out of the laser beam.

In the absence of ponderomotive scattering, the trajectories of the photoelectrons are simply straight lines. Ponderomotive scattering is taken into account by integrating Newton's equations of motion, over 40 ps counted from the time of ejection. As is well known, the ponderomotive force is proportional to the gradient of intensity. The z dependence of the intensity that originates from retardation is taken into account when calculating the gradient.

On their way to the detector, which is located 520 mm away from the focus, the photoelectrons pass through a drift tube. At its entrance they are decelerated by a contact potential with a potential difference δV . The section where the potential difference acts is about 10 mm long. The potential difference δV is 125 mV for $\langle I_0 \rangle = 6.0 \times 10^{13} \text{ W/cm}^2$, 135 mV for $\langle I_0 \rangle = 8.0 \times 10^{13} \text{ W/cm}^2$, and 170 mV for $\langle I_0 \rangle = 1.2 \times 10^{14} \text{ W/cm}^2$. In the simulation the only effect of the potential difference is to decrease the magnitude of the component of the velocity of the photoelectrons along the direction laserfocal-spot-detector. The component in the transverse plane is left unaffected. The potential difference thus slows down the photoelectrons and tends to scatter them off the direction to the detector, the more so the slower they are. Of course, those photoelectrons whose energy is less than δV as they exit the laser beam are stopped by the contact potential.

In the simulation photoelectrons whose velocity vector makes an angle of more than 2.5° with respect to the direction focal-spot-detector, after the potential difference is passed, are not counted as being detected. Otherwise, they are recorded in time bins according to their time of arrival at the detector. The minimum time of flight that is recorded is 15 ns counted from the time the pulse reaches its peak intensity at the focus; there are 1024 time bins, each 2 ns long. Photoelectrons that arrive before 15 ns have elapsed or after $15 + (1024 \times 2)$ ns are discarded. Measurements of angular distributions are simulated by calculating the complete energy spectrum for different angular positions of the detector. Finally, the time-offlight histogram is transformed into an ejection-energy histogram representing the energy spectrum, by converting the limits of each time bin into the corresponding kinetic energies and dividing the yield in each bin by the energy interval it spans.

Typically, for each pulse a little less than 1% of the 20 000 photoelectrons of the random sample contribute to the energy spectrum, if the detector is centered about the polarization direction. The final spectrum is accumulated over 250 laser shots, typically, and is thus based on the times of flight of about 48 000 representative electrons. In general, fewer electrons were detected in the experiment (1-2 per shot).

Figure 7 illustrates the various steps of refinement in the theoretical modeling and their relative importance. It gives the theoretical spectrum for a 0.5 ps pulse at 608 nm with average peak intensity of 8×10^{13} W/cm². For clarity, the curves are offset with respect to each other by 0.5 units in the vertical direction. The top curve (a) uses only the total rate. Consequently only branching into the S = 0 ATI channel is assumed. The next step (b) consists in including the angle-integrated branching ratios [shown in Fig. 6(a)]. This already reproduces all important features of the experimental spectra. In the subsequent three steps only details change, such as, e.g., the energy-dependent resolution, the visibility of certain small peaks, statistical jitter, or the magnitude of the background. This can lead to significant differences in



FIG. 7. Steps of theoretical modeling of the experiment, for a wavelength of 608 nm and intensity of 8.0×10^{13} W/cm². (a) The temporal and spatial variation of the intensity is taken into account and it is assumed that ionization proceeds only into the lowest open ionization channel (S = 0). (b) Additionally, branching into the different ATI channels [as shown in Fig. (6a)] are taken into account. (c) Additionally, depletion of the target and laser shot-to-shot fluctuations are taken into account. (d) Additionally, detector binning and angle-dependent ionization rate [as shown in Fig. 6(b)] are taken into account. (e) Additionally, ponderomotive scattering of the photoelectrons is taken into account. (f) Experimental results.

peak heights in the S = 1 and S = 2 ATI groups. These three steps in refinement are (c) inclusion of depletion and laser pulse shot-to-shot fluctuations (in pulse width and energy), (d) angle-differential detection [in a 5° cone centered on the polarization axis; see Fig. 6(b)], and (e)ponderomotive scattering of the ejected electrons. For comparison (f) shows the measured photoelectron spectrum.

IV. RESULTS AND DISCUSSION

A. Photoelectron energy spectra

Figure 8 shows the experimental (ex) and theoretical (th) photoelectron energy spectra for atomic hydrogen in the energy range from 0 eV to 6.2 eV, at laser wavelengths of 596, 608, 620, and 630 nm, respectively, corresponding to a photon energy between 1.97 and 2.08 eV.

All theoretical spectra shown are calculated without inclusion of laser fluctuations and ponderomotive scattering. As can be seen in Fig. 7 the difference would be very small.

We shall first discuss in detail the spectrum at 608 nm corresponding to a photon energy of 2.04 eV. The average laser pulse peak intensity in the interaction region was 6.6×10^{13} W/cm² and the pulse duration 0.5 ps. The direction of linear polarization of the laser beam was set along the direction of detection of the photoelectrons. To record the spectrum the electron signal was accumulated over 10080 laser shots. The remarks below also apply to the more detailed spectrum shown in Fig. 7, with the modification that the average peak pulse intensity is slightly larger, namely, 8.0×10^{13} W/cm²: here the resonances are labeled to facilitate their identification. In order to classify the resonances observed in the spectrum, we should consider a Floquet energy-level diagram. In Fig. 1 such a diagram is shown together with an MPI process at 608 nm at an intensity of about 3.5×10^{13} W/cm² and the virtual states after absorption of N photons (N = 5, ..., 9). Note that we have kept the threshold energy fixed at E = 0 (that is, we have subtracted the ponderomotive energy from all energy values). For a more precise description, in Fig. 3, we show the real part of the Floquet quasienergies. We see that the shift of the 1s state is indeed very close to P, while the higher Rydberg states hardly at all shift with respect to the threshold. The intermediate states (n = 2, 3) show a complicated Stark shift which also depends on their (dominant) angular momentum. Especially 2s, 3p and 2p, 3s, 3d form systems of strongly coupled states. At zero intensity the energy separation between the n = 2 and n = 3 manifolds of about 1.89 eV nearly equals the photon energy of 2.04 eV.

With the help of these energy curves, the processes contributing to the electron energy spectrum in Fig. 8 (or Fig. 7) are easily understood. The lowest-order ionization process possible for atomic hydrogen at 608 nm. namely, seven-photon ionization, can contribute to the signal in the energy range from 0 eV up to 0.68 eV. According to Eq. (1) the maximum intensity for sevenphoton ionization to be possible is $1.9 \times 10^{13} \text{ W/cm}^2$ (see Fig. 1). At this intensity the photoelectrons leave the atom with 0 eV kinetic energy. If the photoelectrons from the lowest-order ionization process of the atom absorb further photons above the shifted ionization threshold, they contribute to the signal in the energy intervals $[S\hbar\omega, S\hbar\omega + 0.68 \text{ eV}]$, with $S = 1, 2, \dots$ the number of additional photons absorbed. The contribution from intensities less than $1.9 \times 10^{13} \text{ W/cm}^2$ amounts to about 1%of the total signal. Contributions from (7 + S)-photon ionization to the photoelectron spectrum are thus of negligible importance.

At intensities between 1.9×10^{13} W/cm² and 7.7×10^{13} W/cm² the lowest order ionization process is eightphoton ionization [see Eq. (1)]. Photoelectrons from this process have kinetic energies in the range from 0 eV up to $\hbar\omega = 2.04$ eV. The electron energy decreases from $\hbar\omega$



FIG. 8. Excitation wavelength dependence of the photoelectron energy spectrum in the energy range of the lowest three ATI channels (S = 0, 1, 2). The excitation laser wavelength is 596, 608, 620, and 630 nm, respectively, the pulse peak intensity is approximately 6.5×10^{13} W/cm², and the pulse duration 0.5 ps. The upper curves (ex) are experiment, the lower ones (th) theory.

to 0 eV with increasing intensity [Eq. (1)]. In the experiment the average upper intensity was $6.6 \times 10^{13} \text{ W/cm}^2$. corresponding, for eight-photon ionization as the lowestorder process, to an energy of 0.38 eV. Pulse intensity fluctuations of $\pm 1 \times 10^{13}$ W/cm² lead to pulse to pulse fluctuations of the lower photoelectron energy limit in the range from $\sim 0 \text{ eV}$ to 0.76 eV. If additional photons are absorbed above the shifted ionization threshold, the photoelectrons originating from the intensity range from 1.9×10^{13} W/cm² to 6.6×10^{13} W/cm² in the laser pulse appear in energy intervals $[S\hbar\omega + 0.38 \text{ eV}, (S+1)\hbar\omega]$ with $S = 1, 2, \ldots$ Different ATI energy intervals are defined in the spectra Fig. 8 by the energy ranges: S = 0corresponding to E in $[0, \hbar\omega]$, S = 1 corresponding to E in $[\hbar\omega, 2\hbar\omega]$, and S = 2 corresponding to E in $[2\hbar\omega, 3\hbar\omega]$, where S gives the number of photons absorbed above the shifted ionization threshold.

Each one of the ATI photoelectron groups shows a resonance substructure, which is more completely resolved in the S = 0 group than in S = 1, due to the decreasing energy resolution of the time of flight spectrometer with increasing kinetic energy. Such a substructure was first observed by Freeman and co-workers in short-pulse MPI of xenon [6]. It is generated mainly by seven-photon resonant eight-photon ionization in the S = 0 energy range. As can be seen in Figs. 1 and 3, excited states of the atom are shifted into seven-photon resonance during the laser pulse, due to the ac Stark shift in the strong radiation field. The intensity I_R for an m-photon $1s - n\ell$ resonance is

$$m\hbar\omega = E_{n\ell}(I_R) - E_{1s}(I_R). \tag{8}$$

Then Eq. (2) fixes the kinetic energy of the photoelectrons escaping at the resonance intensity. At resonance the ionization rate of the atom may be enhanced and thus a peak appear at the corresponding kinetic energy in the photoelectron spectrum.

Assuming that an excited state does not shift with respect to the threshold energy, the kinetic energy of electrons in the ATI group S generated at resonance is simply given by

$$E_{\rm kin}^S(I_R) = (S+1)\hbar\omega + E_{n\ell}(0) \tag{9}$$

for a state with principal quantum number n shifted into seven-photon resonance. It is completely determined by the binding energy of the unperturbed resonant state, $E_{n\ell}(0)$, and the freqency of the radiation field. The perturbed energy of the excited state enters the relation only if its ac Stark shift is non-negligible.

We used relation (8) to identify excited states which give rise to resonance enhancements in the S = 0, 1, and 2 ATI electron groups in Figs. 7 and 8. For principal quantum numbers $n \ge 5$ the experimentally observed peak positions are identical to the expected (unshifted) positions within the accuracy of the experiment. Only the 4f state (giving the dominant peak in the 608 nm spectrum) shows a slight deviation from the expected position and thus an ac Stark shift somewhat different from the ponderomotive energy of a free electron.

Two significant features in the S = 0 electron group

cannot be attributed with this simple resonantly enhanced multiphoton ionization method, namely, the broad resonance below 1 eV and the small one between the 4f and n = 5 resonances, at 1.34 eV.

The Floquet calculations allow a complete identification of the resonance substructure in the ATI channels. Concerning resonance positions the theoretical electron spectra show a close agreement with the measured ones (see also [25]). Figure 3 reveals an ac Stark splitting of the n = 4 state manifold into an f and a p angular momentum component. The near-zero shift of the 4f state at the resonance intensity is only accidental, since the 4f energy shift with intensity first is negative, but then increases again to become close to zero at the resonance intensity for the 4f state. The 616 nm results can be used to interpret the 608 nm spectrum because the wavelengths are very close. The ac Stark shift of the 4pstate differs from the 4f shift; this results in a resonance position for this state in between the 4f and the n = 5resonances.

According to calculation, the main contribution to the higher n resonances $(n \ge 5)$ comes from the f angular momentum component of the corresponding Rydberg state. In principle all odd angular momentum components may contribute to the seven-photon resonances. The contribution of states with $\ell \ge 5$ for $n \ge 6$ is suppressed by their large centrifugal barrier, which reduces their seven-photon excitation probability from the ground state and also their one-photon ionization probability.

The photoelectron spectrum below 1 eV is, according to theory, strongly influenced by six-photon resonant eight-photon ionization via the "2s" state [14]. This state is shifted into resonance near the pulse peak intensity. It originates from the 2s state but is strongly distorted from a 2s wave function at high field and to stress this point we use quotation marks to identify this resonance as "2s."

The identification of the resonant states by a principal quantum number n and a definite angular momentum ℓ must not be taken literally. One has to bear in mind that the atom is heavily perturbed by the radiation field. The reduced axial symmetry of the system atom plus radiation field means for the resonant states that they will consist of a superposition of either even or odd angular momentum states. All resonant states labeled $(n\ell)$ in Fig. 3 with $n \geq 4$ have a dominant contribution from the corresponding unperturbed atomic configuration at the resonance intensity and can be followed back continuously to the $(n, \ell, m = 0)$ unperturbed hydrogenic state in the limit of vanishing intensity.

The resonances in the spectrum in Fig. 8 appear superimposed on a photoionization continuum which is generated by nonresonant ionization and the overlap of neighbouring resonances. There is also a (small) contribution from MPI of molecular H_2 (which is not present in the theoretical spectra).

The height of the identified resonances decreases strongly with increasing principal quantum number n. Two things are responsible for this behavior. First, the seven-photon excitation and one-photon ionization rates of the resonant states decrease with their principal quantum number. Second, the resonance intensity I_R decreases with n, as can be seen in Fig. 1 or 3. Therefore the resonant ionization probability also decreases rapidly, due to the nonlinearity of the process. Excited states with principal quantum numbers n > 8 contribute only little to resonant ionization at 608 nm (see Fig. 7). States with $n \gtrsim 16$ are not at all expected to contribute individual resolvable resonance enhancements to the spectrum. Classically the electron in these states has a round-trip orbital time which is comparable to or larger than the duration of the excitation laser pulse. Thus in this range of states the electron behaves as if it already were unbound during the excitation process. Stating it another way the spectrum of the excitation pulse overlaps more than one state for $n \gtrsim 16$.

The width of the resonances in the S = 0 ATI photoelectron group is made up of three contributions: the intrinsic width of the resonant ionization process, the residual ponderomotive acceleration of the free electron, and the finite resolution of our time of flight energy analyzer. The n = 4 resonance has a contribution from the ionization process to its width, it is definitely broader than the higher n peaks. Below 1 eV the contributions to the width from ponderomotive scattering or experimental resolution are negligible. The overall shape of the broad peak below 1 eV is determined by the dependence of the ionization rate on intensity near the "2s" resonance and certainly also by the $\pm 1 \times 10^{13}$ W/cm² peak intensity fluctuations of the laser pulses. The second point is important to take into account because the resonance is generated near the pulse peak intensity. Also, the low-energy ends of the spectra are not reliable since low-energy electrons are strongly influenced on their way through the drift tube.

In the energy range from 2.04 eV up the 4.08 eV the photoelectrons have absorbed one additional photon above the shifted ionization threshold. The shape of the spectrum resembles that of the S = 0 lowest-order ATI channel with a reduced energy resolution. An exception is the broad peak below 1 eV; it is not reproduced in the corresponding S = 1 energy range. Thus the higher ATI channels are not a mere reproduction of the S = 0 channel at a lower signal level. This is supported also by the theoretical results.

We shall now compare the spectra at the other excitation wavelengths 596, 620, and 630 nm to the 608 nm spectrum. The laser pulse peak intensity and pulsewidth was similar for all spectra $[0.5 \text{ ps}, (6.5 \pm 1) \times 10^{13} \text{ W/cm}^2$ at 596 nm; 0.5 ps, $(6.6 \pm 1) \times 10^{13} \text{ W/cm}^2$ at 608 nm; 0.5 ps, $(6 \pm 1) \times 10^{13} \text{ W/cm}^2$ at 620 nm; and 0.4 ps, $(6.5 \pm 1) \times 10^{13} \text{ W/cm}^2$ at 630 nm]. At 596 nm the signal was accumulated over 9.000, at 620 nm over 10.000, and at 630 nm over 12.000 laser shots. All four spectra show the energy range of the lowest three ATI channels S = 0, 1, and 2. In a similar way as at 608 nm the identified states at all wavelengths are f states. The 4p state between n = 4 and 5 appears only at 608 nm and 620 nm. It does not rise above the noise level at 596 nm and 630 nm.

At 596 nm, seven-photon ionization can contribute to the electron yield up to 0.96 eV. The intensity where seven-photon ionization crosses over to eight-photon ionization is here quite large at 2.8×10^{13} W/cm². Eightphoton ionization with six- and seven-photon resonant intermediate states contributes only in the energy interval [(0.85 ± 0.3) eV, $\hbar\omega$] with the photon energy $\hbar\omega = 2.08$ eV. This means, that there is probably an appreciable contribution from seven-photon ionization to the broad yield enhancement below 1 eV in this case. It appears that an increasing ionization rate with decreasing photoelectron kinetic energy (because intensity increases in this direction) in combination with a decreasing electron detection efficiency below ~ 0.5 eV is responsible for the broad yield maximum below 1 eV. In this case it is not necessary to assume resonant states to enhance the ionization rate.

The dominant contributions to the spectrum above 1 eV are generated by the 4f and 5f resonances. Higher n states contribute with rapidly decreasing amplitude towards the boundary between the S = 0 and S = 1 ATI channels.

In the spectra taken at longer wavelengths contributions from seven-photon ionization to the S = 0 ATI channel are negligible. Here the S = 0 energy range is dominated by eight-photon ionization with the six- and seven-photon resonances (as discussed before) appearing. Only at 630 nm besides eight-photon also nine-photon ionization contributes to the electron yield in the energy interval [1.26 eV, $\hbar\omega$] ($\hbar\omega$ = 1.97 eV). Pulse peak intensity fluctuations give rise to fluctuations of the lower bound of this interval in the range from 1.26 eV up to 1.97 eV. The crossover from eight- to nine-photon ionization is located at an intensity $I=5.65\times 10^{13}~{\rm W/cm^2},$ an appreciable amount below the average pulse peak intensity $(6.5 \pm 1) \times 10^{13}$ W/cm². In the energy interval for nine-photon ionization, eight-photon ionization at intensities from 0.47×10^{13} W/cm² up to 2.32×10^{13} W/cm² contributes to the electron yield. The corresponding intensities are less than half the intensity where only ninephoton ionization is possible $(I \ge 5.65 \times 10^{13} \text{ W/cm}^2)$. Additionally the crossover intensity to nine-photon ionization is quite low, so that ground state depletion is certainly not complete. From these facts one may expect nine-photon ionization to contribute measurably to the electron yield in the energy range [1.26 eV, $\hbar\omega$].

The nine-photon ionization process can be enhanced by eight-photon resonances with excited states having a principal quantum number $n \geq 5$. These resonant states are distinct in character from states which enhance eight-photon ionization after absorption of sevenphotons in the same photoelectron energy range. They are composed of even angular momentum states, while the seven-photon resonant states are odd angular momentum states. The sharp spikes visible in Fig. 4 in the upper right-hand corner are given by resonances with dominantly ng angular momentum states, i.e., $\ell = 4$, with $n \geq 5$.

The experimental spectrum at 630 nm gives a hint that really nine-photon ionization contributes to the electron yield in the energy range [1.26 eV, $\hbar\omega$]. First, the mean signal increases when $\hbar\omega = 1.97$ eV is approached from below, while in all the other spectra it decreases. Sec-

ond, the height of the n = 5 resonance decreases with respect to the 4f resonance in going from 596 nm to 620 nm excitation wavelength, while it increases relative to the 4f resonance again at 630 nm. This increase may be through the possibility of eight-photon resonant ninephoton ionization via the 5g state in the high intensity range of the laser pulses at 630 nm. A dramatic increase of the electron yield at the eight-photon resonances relative to the 4f seven-photon resonance is prevented by depletion of the hydrogen ground state in the intensity range of eight-photon ionization. A further increase in wavelength to 638 nm, where the energy of seven photons coincides with the zero external field ionization threshold of atomic hydrogen (13.6 eV), would probably lead to nine-photon ionization dominating the S = 0 ATI channel at least in the upper half, if the pulse peak intensity were to increase beyond 5.2×10^{13} W/cm². Then eight-photon resonances are expected to dominate over seven-photon resonances for states with principal quantum numbers $n \geq 5$. Here ground state depletion will certainly not suppress eight-photon resonances.

The most prominent change in the photoelectron spectra in going from 596 nm to 630 nm is in the relative strength of the broad peak below 1 eV with respect to the nf resonances. With increasing wavelength this peak, which at 608 nm is generated by the "2s" resonant intermediate state, gains in significance with respect to the higher n resonances. At 630 nm it becomes the strongest resonance in the S = 0 ATI channel. We see a similar behavior in the calculated total electron yield. One contribution to this change probably originates in the increasing space-time volume in the laser pulse, where the "2s" state is resonant, in going from 608 nm to 630 nm with respect to the corresponding volume for the nf states. At 608 nm only a small spatial volume near the beam axis and times near the pulse maximum can contribute to the "2s" resonance, while at 630 nm this volume and time interval have expanded. Additionally, besides the "2s" state, the "3p" state will increasingly contribute to the electron yield enhancement with increasing wavelength near the intensity where eight-photon ionization crosses over to nine-photon ionization. This fact also tends to increase the resonance below 1 eV with respect to the nf resonances. The attribution of 3p to this resonance is even more doubtful than for the "2s", since—as can be seen in Fig. 3—the "3p" dips below the threshold around $I = 1.3 \times 10^{13} \text{ W/cm}^2$ and we cannot be sure of its attribution at higher intensity.

At 630 nm the photoelectron spectrum clearly shows that the S = 1 ATI channel is not merely an identical reproduction of the S = 0 channel at a lower signal level. The broad "2s/3p" resonance is higher than the 4f resonance in the S = 0 channel but in S = 1 the relative heights of the corresponding resonances are reversed. There may not be any simple explanation for this feature. One may certainly assume the spatiotemporal volumes which contribute to the respective resonances in S = 0and S = 1 to be approximately the same. Therefore one would expect the ratio of the "2s/3p" peak height to the 4f peak height in the S = 1 channel to be even higher than in the S = 0 channel, because the "2s/3p" resonance intensity is higher than the 4f one with a correspondingly higher probability to absorb a further photon above the ionization threshold on the "2s/3p" resonance. Yet both the experimental and theoretical results show just the opposite behavior.

The variation of the excitation wavelength at otherwise approximately constant conditions shows that the MPI process changes quite strongly. In the photoelectron spectra relative peak heights in the resonance substructure change. Also the order of the ionization processes, contributing to the electron yield, for example, in the S = 0 ATI channel, varies.

The theoretical results agree with the experimental ones down to a very fine level of detail, including peak positions, widths, and relative heights. The notable exceptions to this agreement are (i) the experimental data have a significant "background" compared to the theoretical ones and (ii) the branching ratios into the three ATI groups shown do not agree: the theory gives much higher rates into the S = 1 and S = 2 groups compared to the S = 0 group than the experiment. What might account for this discrepancy is the neglect of transfer of population to dressed excited states in our calculation (see the discussion in Sect. III A above). Unfortunately, we are not able at present to obtain numerically reliable branching ratios for the resonance states at the required intensities. Population left in excited states at the end of short pulses has been observed in xenon [3]. In the case of hydrogen, however, the gaps at avoided crossings are very narrow—and in fact the crossing with the 4f dressed state is not avoided in the real part. This suggests that adiabatic transfer of population to dressed excited states is less effective here than in the recent experiments in xenon [26] or potassium [27]. Moreover, for our hydrogenic case we expect any population in the dressed 4f, 5f, or 6f states to decay promptly after transfer from the dressed 1s state, because the lifetimes of these states at the crossings are only a few optical field cycles (e.g., the lifetime of the 4f state at the crossing in Fig. 5 is 2.5 fsec). This makes it unlikely that a substantial fraction of the atoms be left in one of these excited states at the end of the pulse [28].

The 608 nm data have also been studied theoretically within the resolvent formalism, by Gontier and Trahin [18]. They presented yields in photoelectrons integrated over the intensity distribution of a realistic laser pulse, but only for an energy within the first (S = 0) ATI peak (i.e., below 2 eV). Their results are in overall agreement with ours. There are, however, small but significant differences in the intensities at which Stark-shift-induced resonances occur, and therefore in the position of the resonance peaks in the energy spectrum.

B. Photoelectron angular distributions

The minimal resonant MPI model of Fig. 1 gives no clue on the angular momentum of the resonant states, since the ponderomotive shift is independent of angular momentum. Only a measurement of the angular distribution of the photoelectrons on the resonances may give a hint on ℓ .

In a short-pulse photoionization experiment, the photoelectrons suffer almost no ponderomotive scattering in the laser focal spot. When the pulse is gone they therefore have the same velocity distribution that they had when they were created in the photoionization process. This means that the photoelectron angular distributions one measures are identical to the angular distributions the electrons had when they were ejected from the atom. Measuring an energy-resolved angular distribution even selects a certain intensity in the radiation pulse at which the photoelectrons have been released by the atom. Such an angular distribution is proportional to the partial ionization cross section of the atom.

For linearly polarized light the partial ionization cross section $d\sigma(E, \theta)/d\Omega$ at the photoelectron kinetic energy E is only a function of the angle θ between the polarization direction of the light and the direction of emission of the photoelectron. It can be expanded into a sum over spherical harmonics $Y_{\ell 0}(\theta, \varphi)$ [29], which to lowest order proceeds up $\ell = N$, where N denotes the number of photons absorbed. In addition for atomic hydrogen with its 1s ground state the summation is either only over even ℓ values for an even number of photons absorbed or otherwise only over odd ℓ values. Intermediate resonances or near resonances with bound excited states with a definite angular momentum may influence the angular distributions through especially large or small coefficients for certain ℓ .

For sake of signal the measured energy-resolved angular distributions $S(E, \theta)$ are integrals of the signal over small energy intervals Δ . $S(E, \theta)$ is related to the partial ionization cross section $(d\sigma/d\Omega)$ through

$$S(E,\theta) = \alpha \int_{E-\frac{\Lambda}{2}}^{E+\frac{\Lambda}{2}} dE' \int_0^\infty dE'' f(E'') \frac{d\sigma}{d\Omega} (E'-E'',\theta) \delta\Omega$$
(10)

with f(E) the instrument function of our energy analyzer and $\delta\Omega$ the solid angle of detection. The interval Δ is usually chosen to be equal to the total width of a particular resonance peak in the photoelectron spectra. $S(E, \theta)$ is proportional to $(d\sigma/d\Omega)$ if the partial cross section does not change much over the interval Δ and over the energy range where f(E) is appreciably different from zero.

Figure 9 shows energy-resolved angular distributions in the S = 0, 1, and 2 ATI channels recorded at the excitation wavelengths 608 nm and 620 nm. The laser pulse peak intensity was $(7\pm1) \times 10^{13}$ W/cm² at 608 nm and $(6\pm1) \times 10^{13}$ W/cm² at 620 nm. In both cases the pulse duration was 0.5 ps. All angular distributions were measured at resonances and are identified by the quantum numbers $(n\ell)$ of the corresponding resonant state. The signal integration interval Δ always extends over the complete range of the resonance. Especially for 2s it is the total experimental energy range below ~ 1 eV electron kinetic energy (see Fig. 8). The full lines in Fig. 9 are the theoretical results, from our simulation (without inclusion of ponderomotive scattering).

The angular distributions at 608 nm and 620 nm look very similar and also change in a similar way from one resonance to the other. Therefore we will discuss them in the following by means of the 608 nm results.

All angular distributions in the S = 0 channel show a more or less pronounced maximum at $\theta = 90^{\circ}$. This behavior is a clear evidence for absorption of an even number of photons producing the electron signal in the S = 0 ATI channel, at least at the resonances investigated in Fig. 9. In connection with the electron energy spectra we already found eight-photon ionization to be responsible for the electron yield in the S = 0 ATI electron group based on energy considerations. This is thus confirmed by the angular distributions.

As noted above, the energy-resolved angular distributions at resonances may give a hint on the angular momentum of the resonant intermediate state, as far as a definite angular momentum can yet be assigned to it at the resonance intensity [11]. For MPI of xenon an identification of the angular momentum of resonant states was for example possible [11]. At the intensities and wavelengths in Fig. 9 all states except "2s" are seven-photon resonant and the absorption of one further photon ionizes the atom leaving the electron in the S = 0 ATI channel. If now the angular distribution is dominated by a partial wave with angular momentum ℓ , the resonant state, according to the dipole selection rule, should have $\ell' = \ell \pm 1$. A propensity rule favoring $\Delta \ell = +1$ transitions in the ionization step [30] then even restricts the angular momentum of the resonant state to $\ell' = \ell - 1$.

The angular distribution at the "2s" resonance does not show any pronounced substructure. A 2s six-photon resonant intermediate state would favor a d partial wave



FIG. 9. Energy-resolved angular distributions of the photoelectrons measured at the resonances in the S = 0, 1, and 2 ATI channels for two different wavelengths 608 nm and 620 nm. The dots represent the experimental electron yield and the lines the theory. The yield is normalized to 1 at $\theta = 0^{\circ}$.

dominating the outgoing electron wave function. This is definitely not the case in Fig. 9. As already discussed, the "2s" state at the resonance intensity does not have much in common with the unperturbed 2s state of the hydrogen atom. Different angular momenta are mixed into this intermediate state and lead to the rather structureless angular distribution observed for the leaving photoelectrons.

Besides the main lobe at 0° the series of f resonances with $n = 4, \ldots, 6$ shows one further clear maximum in the angular distribution for $\theta \leq 90^{\circ}$. For the 4f intermediate state this maximum appears near $\theta = 45^{\circ}$. With increasing principal quantum number n it slightly shifts to a smaller angle, reaching $\theta \sim 40^{\circ}$ for 7f. The g partial wave and, with increasing n, an increasing amount from an i partial wave contribute to the angular distribution. No pure g wave dominates as one might expect according to the propensity rule for one photon ionization of fstates. Again, one must note that at the resonance intensities $(I > 10^{13} \text{ W/cm}^2)$ the atom is distorted and the state identification as nf states only means that the nfwave function dominates the true wave function. Contributions from other angular momenta $(\ell \neq 3)$ to the wave function of the resonant state will lead to a deviation of the photoelectron angular distribution from a pure gpartial wave, as observed in experiment and theory.

A further effect contributes to washing out the g wave in the continuum: with increasing principal quantum number one would expect the resonant state wave function to approach a pure nf function and the corresponding resonant angular distribution to approach g partial wave character. However, as can be seen in Fig. 4, the resonance enhancement of the electron yield above the background ionization decreases with increasing n. Therefore one expects angular distributions to be increasingly influenced by the background. The increasing mean ionization rate on which the resonances are superimposed is responsible for the observed background ionization in the experiment. It may give rise to the increasing deviation of resonant angular distributions from a g wave distribution with increasing principal quantum number. Apart from background contributions np resonant states with $n \geq 5$, not resolved from the nf resonances, will also influence the measured resonant angular distributions.

Not always do the energy-resolved angular distributions give the correct indication on the dominant angular momentum of the excited state involved in the resonance. For example, at the small "4p" resonance peak, the theoretical angular distributions were calculated at 596 and 608 nm, and found to be, for the eight-photon ionization (S = 0) channel, similar to the ones for the 4fand 5f resonances. (They are not similar in higher ATI channels.) One would have expected, instead, that the angular distribution be dominated by the d wave since the 4p resonance clearly coincides with a crossing in the quasienergies of the dressed 1s state and of a dressed state starting in the weak field as the 4p state, whose wave function at the resonance still has dominantly pcharacter (its f-wave component is not negligible, however). We regard the similarity in the S = 0.4f and 4pangular distributions as somewhat coincidental; it may



FIG. 10. ATI channel integrated photoelectron angular distributions, taken at an excitation wavelength of 608 nm, a pulse peak intensity of 1×10^{14} W/cm², and a pulse duration of 0.5 ps. The dots represent the measurement and the full lines are fit curves to the data.

be due to the fact that the 4p resonance is much smaller (and narrower) than the 4f resonance (experimentally, the 4p resonance is visible as a peak only at $\theta = 0$), and we conclude that an energy-resolved angular distribution is not always a good guide for characterizing a resonance enhancement.

Gontier and Trahin calculated angular distributions at 608 nm excitation wavelength taking into account resonance enhancement after absorption of seven-photons at a definite intensity [17]. In the calculation only s, d, and g partial waves were used to represent the wave function of the leaving electron in the S = 0 ATI channel after absorption of eight photons. Their results for the 5f resonance are in fair agreement with our results.

Figure 10 shows measured angular distributions $S_S(\theta)$ integrated over ATI channels for S = 0, 1, 2. These ATI channel selective angular distributions $S_S(\theta)$, where the index S numbers the ATI channel, are related to the differential ionization cross section through

$$S_{S}(\theta) = \alpha \int_{S\hbar\omega}^{(S+1)\hbar\omega} dE \frac{d\sigma}{d\Omega}(E,\theta), \quad S = 0, 1, 2, \dots$$
(11)

In this case the instrument function f(E) is unimportant. The solid line is a fit to the data; we used only the lowestorder harmonics up to $\ell = 6$.

The excitation wavelength was $\lambda = 608$ nm. The pulse peak intensity in this measurement was $(10 \pm 1.5) \times 10^{13}$ W/cm^2 at a pulse width of 0.5 ps. We used a higher pulse intensity to have a good signal statistics in the higher ATI channels. At this intensity eight-photon ionization contributes to the electron yield in S = 0 in the whole energy range $[0, \hbar\omega]$ and in addition nine-photon ionization in the range [1.2 eV, $\hbar\omega$], that is, starting with the 4f resonance. Then nine- and ten-photon absorption contributes to S = 1 and ten- and eleven-photon absorption to S = 2 in the corresponding energy ranges. At $\theta = 90^{\circ}$ a maximum in the electron yield appears in S = 0 and S = 2 and a minimum in S = 1. This indicates that for each ATI channel the lower-order process dominates photoionization, i.e., eight-photon ionization for S = 0 and (8 + S)-photon absorption for the higher ATI channels. Depletion of the ground state in the eight-photon ionization process is certainly responsible for this behavior. The maximum appearing in the angular distributions on the f resonances near $\theta \sim 45^{\circ}$ (see Fig. 9) appears suppressed in $S_0(\theta)$. The contribution of the quite structureless "2s" resonance to $S_0(\theta)$ is certainly responsible for this suppression.

The number of oscillations in $S_S(\theta)$ increases with S. This means that increasingly higher partial waves contribute to the angular distribution. Thus preferred $\Delta \ell = +1$ transitions, i.e., the propensity rule for ionization mentioned above, govern the ATI process. We already observed such a behavior in long pulse (~ 5 ns pulse duration) MPI of atomic hydrogen at 532 nm [19]. The ATI channel integrated angular distributions $S_S(\theta)$ for short laser pulses should just correspond to the angular distributions one measures with long pulses, if the influence of ponderomotive scattering on angular distributions can be neglected and the ionization process of lowest possible order dominates each ATI channel.

V. CONCLUSIONS

Atomic hydrogen and xenon seem to be the best candidates to investigate the influence of resonances on photoionization in a high-intensity subpicosecond laser pulse within the visible spectral range. At low light intensity both atoms are ionized after the absorption of about seven photons. For a subpicosecond pulse an ionization process of this order requires an intensity higher than $\sim~10^{13}~{
m W/cm^2}$ to give rise to an appreciable ionization probability of the atom. In this intensity range ac Stark shifts of excited states relative to the ground state reach a value comparable to the photon energy $\hbar\omega$. This large shift implies that regardless of a detuning of excited states from m photon resonance these states are dynamically shifted into resonance at a certain intensity within the pulse. The dynamical resonance may then enhance the photoelectron yield. To identify such a resonance its width has to be small compared to the photon energy. This condition is satisfied for some of the excited states of atomic hydrogen and xenon. An atom with an appreciably higher ionization threshold may not allow the observation of a resonance enhancement for visible laser pulses ($\lambda \sim 600$ nm). When excited states are first shifted into m photon resonance, the ionization rate of such an atom may be too low to observe ionization. If at a much higher intensity $(I > 10^{14} \text{ W/cm}^2)$ these excited states shift again into resonance, their ionization width will probably be too large for the resonance to produce an identifiable enhancement in a photoelectron spectrum. It is likely that an atom with an ionization threshold appreciably lower than for xenon or hydrogen will get ionized with probability one before the intensity reaches a level where excited states are shifted into resonance, at least for large enough a detuning from excited states.

We investigated the MPI process of atomic hydrogen in an intensity range near 10^{14} W/cm² and wavelengths around 600 nm. Under these conditions the photoelectron spectra show that ionization is dominated by resonant processes. Under our experimental conditions sixand seven-photon resonances enhance the electron yield.

The main contribution to the S = 0 ATI channel is then eight-photon ionization. At the pulse duration of 0.5 ps an increase in peak intensity does not change this situation appreciably. Depletion of the ground state during the rising part of the pulse prevents nine-photon ionization to dominate the S = 0 ATI electron group in the high-intensity range, where this is the lowest-order ionization process. The photoelectron spectra we measure show a distinctive dependence on the excitation wavelength near 600 nm. There is one definite difference between the measured photoelectron spectra and the calculated ones: in the experiment the 4f resonance in the S = 0 ATI channel is always higher than the corresponding one in the S = 1 channel after absorption of one further photon at all excitation wavelengths and laser pulse peak intensities. This results in the overall electron yield in the S = 0 channel being higher than the yield in the S = 1 channel. At 608 nm excitation wavelength the calculation shows just the opposite behavior (see also [25]). This discrepancy between theory and experiment may be due to our simplification of theoretically treating ionization as proceeding from a single Floquet state.

In contrast to MPI of xenon [11] the energy-resolved angular distributions at the resonances in the S = 0 ATI channel do not allow one to assign a definite angular momentum to the resonant intermediate state. A reason for this may be the ℓ degeneracy of the excited hydrogen states, which may give rise to a stronger mixing of different angular momenta in the perturbed states at the resonance intensity. We have performed detailed comparisons between experimental and theoretical spectra and have obtained satisfactory agreement, even for energyresolved angular distributions.

It would be interesting to see the influence of a further laser pulse width reduction below ~ 0.5 ps on the MPI photoelectron spectra of atomic hydrogen. It may, for example, allow nine-photon ionization to dominate the S = 0 ATI channel in the appropriate intensity range, because depletion of the ground state may be suppressed in this way. Then the corresponding eight-photon resonances should be detectable in the photoelectron spectrum. Such a pulse width reduction will probably also result in high n resonances to disappear. For example, for a 100 fs pulse the classical orbiting period of an electron in a state with principal quantum number n = 8nearly equals the interaction time. Thus resonances with $n \sim 7$ should disappear from the photoelectron spectrum.

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