Giant Stark Shifts in Multiphoton Ionization

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We report photoelectron energy spectra from multiphoton ionization of xenon by 150-fs pulses wavelength tuned between 575 and 675 nm. The spectra show a number of structures that are interpreted as Stark-induced resonances. Measuring the energy of these structures for different wavelengths yields the intensity and wavelength dependencies of the corresponding Stark shifts. For intensities up to 3×10^{13} W cm^{-2}, states between $7p$ and $6f$ were found to undergo giant shifts (up to 1.5 eV). These results are compared with the predictions of a second-order perturbation calculation.

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One of the most surprising results in multiphoton ionization of atoms is the recent discovery[1] of structures in the photoelectron energy spectra taken with subpicosecond pulses. These structures are completely different from those usually obtained with long pulses: Each peak of the standard above-threshold ionization (ATI) spectrum splits into a number of substructures separated by amounts differing from the photon energy. The scenario that has been proposed[1] to explain such structures sheds new light on multiphoton-ionization processes, especially by implying that such processes are, in fact, always resonant, as soon as the intensity is high enough. The observations by the AT&T group[1] have been subsequently confirmed by ourselves[2] and Feldman and colleagues.[3] The key idea is the following: In the intense electromagnetic field, all the atomic energy levels are Stark shifted. When the energy of a particular level becomes equal to the energy of an integer number of photons, the ionization probability is boosted. The photoelectron which is released at precisely this intensity of the light has a corresponding quiver energy (on top of its drift kinetic energy) which is *lost* if the pulse *turns off before* the electron has significantly moved.[4] Subpeaks therefore appear in the electron energy spectrum at energies down shifted (compared to the long-pulse situation) by amounts only determined by the intensity at which each resonance is adjusted.

This scenario has been supported by three experimental findings: (i) The measured positions of the substructures reproduce (more or less) the known xenon energy levels;[1,2] (ii) the substructures do not appear either when light is circularly polarized[2] or the pulse is too short to allow a buildup of the resonance;[5] (iii) the energies of the substructures do not depend on the pulse peak intensity. Because of this last property, it is impossible to explore the intensity dependence of the involved Stark shifts at a single laser wavelength. However, the detuning from a resonance, and, consequently, the intensity required to induce it, can be adjusted by changing the wavelength. Therefore, following the energy of a given substructure as the wavelength is scanned actually provides a measurement of the Stark shift as a function of intensity. Furthermore, adjusting the energy of a given number of photons below or above the energy of a given state will suppress the corresponding substructure depending upon whether the corresponding Stark coefficient is positive or negative, respectively.

The specific case investigated here is the seven-photon ionization of xenon involving Stark-induced six-photon resonances. The experimental setup has been described before.[2,4,5] We just recall here that we use a time-of-flight spectrometer with a collection efficiency of 50% and a resolution of 30 meV. The central experimental requirement in this work is the availability of high-peak-power femtosecond pulses with the potential of large tunability. This was obtained by using the technique of the amplification of the continuum.[6,7] To summarize, the output beam of the laser previously described[2,4,5] is focused into a 2-cm-long water cell to produce a white-light continuum from which an interference filter selects a narrow band. We use a set of filters with bandwidth compatible with a 100–150-fs duration. Coarse tunability is obtained by choosing the appropriate filter while fine tunability is achieved by turning the filters. The beam undergoes a first amplification in a dye cell pumped by the same Nd-doped yttrium aluminum garnet laser, passes through a spatial filter, and finally undergoes a double-pass amplification in a second cell. The beam is again spatially filtered and a final aperture selects the central uniform spot. The wavelength range of this experiment was covered by several dyes, namely, rhodamine dyes (560,590,610) and DCM [4-(dicyanomethylene)-2-methyl-6-(*p*-aminostyryl)-4H-pyran]. The pulse spectrum was monitored in real time by a 0.25-m spectrograph and an optical multichannel analyzer. This beam was focused into the vacuum chamber by a 13-cm

achromatic lens securing up to 5×10^{13} W cm^{-2}.

If E_P the photon energy, E_I the unperturbed ionization potential, E_R the unperturbed atomic energy, and I the intensity, then the M-photon resonance condition and the electron energy E at which the corresponding structure appears in an N-photon ionization are, respectively,

$$ME_P = E_R + (\alpha_r + \alpha_i)I - \alpha_g I\,, \tag{1}$$

$$E = NE_P - E_I - \alpha_p I - \alpha_g I + \alpha_i I\,, \tag{2}$$

where $\alpha_r I$, $\alpha_g I$, and $\alpha_i I$ are the ac Stark shifts of the resonant state and the atom and ion ground states, respectively. α_p is the intensity coefficient of the quiver energy, $e^2/2\epsilon_0 m\omega^2$. In (1) and (2) all the intensity dependences have been assumed linear but it is not necessarily so and, in fact, some nonlinearity can be expected at such intensities.[8] Let us call E_0 the electron energy that would be observed for an N-photon ionization in a long-pulse experiment, $E_0 = NE_P - E_I$. In the particular case of xenon, the static polarizabilities of the XeI and XeII ground states are, respectively, 0.04 and 0.03 in units of cm^{-1}/GW cm^{-2}. The difference, which appears in (1) and (2), can therefore be neglected since α_p is 0.28 in the same units.[9] Eliminating I between (1) and (2) yields the perturbed energy of the resonant state,

$$\tilde{E}_R = ME_P = E_R + \frac{\alpha_r}{\alpha_p}(E_0 - E)\,. \tag{3}$$

A plot of ME_P as a function of $E_0 - E$ will show a straight line with slope α_r/α_p and intercept E_R *if* α_r/α_p *is independent of* E_P. This plot represents the variations of the state energies as a function of I/E_P^2, where I is *not* the peak laser intensity, but the one necessary to tune the resonance in Eq. (1).

Figure 1 shows a typical electron energy spectrum taken at 600 nm. On this spectrum is indicated the value of E_0 as well as some values of $E_0 - E$. Similar spectra have been taken from 575 to 675 nm. From 575 to 585 nm, the spectra are dominated by the six-photon ionization with small substructures due to five-photon resonances. From 585 to 600 nm, spectra with more complicated features appear, possibly because of resonances with autoionizing states lying between the $P_{3/2}$ and the $P_{1/2}$ thresholds. In this paper we will concentrate on the range 600 to 670 nm. In this range, the energy of six photons crosses the $P_{3/2}$ threshold. However, the intensity-induced shift is such that the six-photon ionization is suppressed. The center of gravity of the seven-photon ATI "peak" is down shifted by approximately 1.2 eV (see Fig. 1) and displays a number of substructures. For each laser wavelength, the quantities $E_0 - E$ are measured and plotted as a function of $6E_P$. The result is summarized on the graph of Fig. 2. An offhand assignment of these peaks would be impossible, but some prominent features can be tracked continuously from one experiment to the other and make it possible to relate experimental points of Fig. 2 to each other. In the first approximation, the experimental points reasonably fall on straight lines which, when extrapolated to zero shift, point to energies equal to the energies of atomic states from $7p$ to $10p$ and $4f$ to $6f$ within the experimental uncertainty (less than 100 meV). The slopes given by least-squares fits to linear functions are all close to one. This means that the second-order Stark coefficients α_R are very close to α_P. This is not a surprise for f states or for states with a high principal quantum number. How-

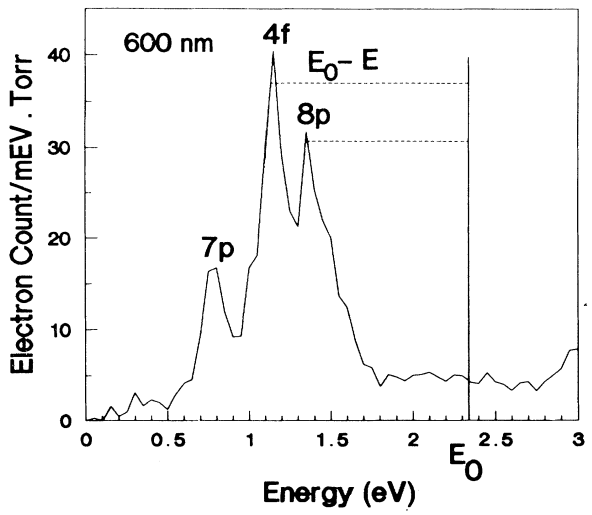

FIG. 1. Typical electron energy spectrum taken at 600 nm. E_0 is in this case 2.34 eV. The substructures described in the text are labeled according to the final assignments.

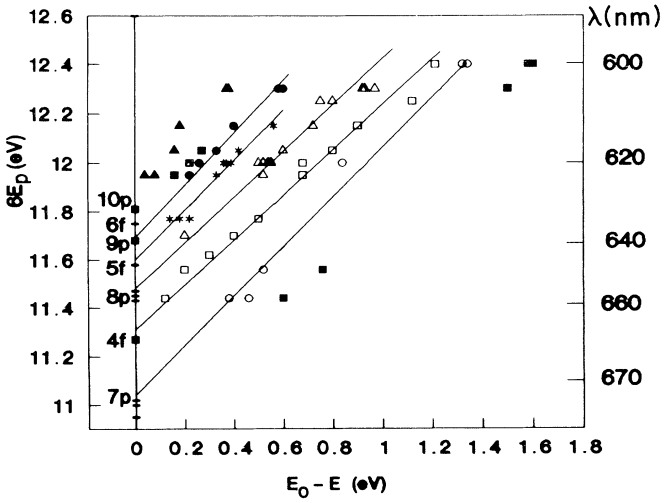

FIG. 2. Plot of $6E_P$ as a function of $E_0 - E$. For clarity, only a few lines have been drawn as guides to the eye. The filled squares below the line corresponding to the $7p$ state may be assigned to the $6p$ but do not extrapolate to the zero-field position of this state.

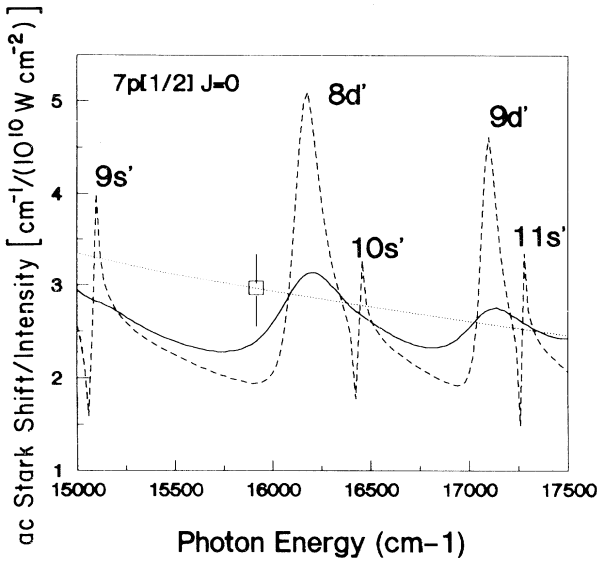

FIG. 3. Result of a second-order Stark-shift calculation of $7p[\frac{1}{2}]$ $J=0$ state as a function of the photon energy (dashed line). The dotted line is the ponderomotive shift. The solid line is the shift convoluted with the laser linewidth. The vertical scale is in $cm^{-1}/(10^{10}\ W cm^{-2})$ units. An experimental value deduced from our results is shown (expressed in the same units).

ever, this simple behavior was not expected for states like the $7p$ which are about one photon away of states (like autoionizing states) to which they are dipole coupled. In an attempt to bring physical ground to our analysis of the experimental data, we have performed a calculation of the second-order ac Stark shifts of some even-parity excited states in xenon. We use wave functions derived from a multichannel quantum-defect analysis of Rydberg series of Xe described elsewhere.[10] Figure 3 shows, for example, the shift of the $7p[\frac{1}{2}]$ state (solid line) as a function of the photon energy. The structures are due to autoionizing resonances below the $^2P_{1/2}$ threshold. The dotted line indicates the ponderomotive term. The dashed line is a result obtained by convoluting with a Lorentzian function with a 150 cm^{-1} width at half maximum (equal to the laser bandwidth). The conclusion of the calculation is that most of the excited states have shifts close to the ponderomotive value. Even the $7p$ state, which is influenced by autoionizing resonances, has an *average* shift close to this value. The essential assumption for the tentative assignment of the observed substructures (Fig. 2) is that the variation of the light shift is essentially the same as in the zero-field limit. Our measurements clearly show that this is true *throughout the intensity range used in the experiment.* The question, however, remains whether this statement can be continuously extended from the low-intensity region where a second-order calculation is undoubtedly valid, to the high-intensity region covered here. It could very well be that a simple behavior is *recovered* at high intensities. This last interpretation seems to be supported by Floquet-type calculations of the ac Stark shifts.[11] In this case, extrapolation of the experimental shifts towards the low-field limit would only be possible *diabatically* (by this we mean jumping over possible avoided crossing between Stark-shifted states), and the states identified as $7p, 4f, \ldots$, would turn at high intensities into strong mixtures of different atomic states.

In conclusion, this experiment supports the resonance interpretation of the substructures appearing in the photoelectron energy spectra. Assuming the validity of this scenario, it has allowed for the first time to follow the energies of atomic states as a function of laser intensity up to 3×10^{13} $W cm^{-2}$. It appears that the shifts are linear, and close to what the perturbation theory predicts, to the precision of the experimental data. The Stark coefficients are close to the ponderomotive one even for the state identified as the $7p$. This behavior is close to that predicted by second-order Stark-shift calculations when averaged over the structures due to autoionizing states. The method used here is, to our knowledge, the only one which allows to extend Stark-shift measurements[12,13] to such intensities.

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