# Laser Intensity for Maximum Yield in Multiphoton Ionization

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An optimum laser intensity that maximizes the photoionization yield is found in a two-photon resonant, three-photon ionization experiment. At laser intensities higher than this optimum, a negative value is obtained for the exponential index describing this multiphoton process, both at zero detuning and at the detuning for which the signal is maximized. Despite the presence of large ($>1$ Å) optical Stark shifts, Gaussian beam-focusing effects produce an excitation spectrum peaked near zero detuning and reverse the sense of its skewness.

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The experimental configuration of two lasers focused into a cell is of general relevance to laser chemistry and isotope separation. Typically, one laser is relatively narrowband to provide selectivity, while the second is not necessarily narrowband but is intense so as to ionize all of the atoms selected by the first. If the laser beams are not too intense, simple perturbation theory can be used to describe the process. If, on the other hand, the lasers are intense, the effects of line broadening,[1] ac Stark shifts,[2] and Gaussian beam focusing[3] play a crucial role in the process. In order to optimize the ion yield in a given experiment, all of these effects and their interplay must be taken into account. In this Letter, we describe a two-photon resonant, three-photon ionization experiment in which the effect of the ac Stark shift is so large that, at sufficiently large laser intensity, the yield of photoions actually decreases with increasing laser intensity. This occurrence implies the existence of an optimum laser intensity to produce the maximum yield of photoions. We find very good agreement between our experimental data and theory. However, our measured cross section is $\sim 20$ times larger than that measured in a previous experiment[4] conducted at much lower atomic number densities and lower laser intensities. Photoionization cross sections are normally assumed to be intensity independent; however, at high laser intensities and high number densities, above-threshold ionization[5] can occur, leading to an intensity dependence of the measured cross section.

In our experiment, a low-intensity laser resonantly excited the atoms in a sodium vapor cell from the $3s$ to the $5s$ state via two-photon absorption. A second, more intense laser nonresonantly ionized the excited atoms. The rapid photoionization induced by the nonresonant field causes lifetime broadening of the resonantly excited $5s$ level, while the ground state is Stark shifted predominantly by the same nonresonant field (see inset to Fig. 2). Both fields were of duration $\sim 4$ ns and were produced by dye lasers pumped by an excimer laser. The laser that was tuned to the two-photon resonance at 6022 Å operated with a bandwidth of $\sim 2$ GHz and an intensity, $I_R$, in the range 1 to 10 MW cm$^{-2}$. The second laser operated at $\sim 7000$ Å, beyond the molecular absorption bands, and operated with an intensity, $I_{NR}$, in the range 0.01 to 10 GW cm$^{-2}$. Both lasers were tightly focused to a spot size of approximately 20 $\mu$m within a 25-mm-long cell containing $\sim 4\times 10^{14}$ sodium atoms/cm$^3$. A weak electric field was applied between two plates within the cell in order to collect the photoions. For a particular two-photon-resonant laser intensity, the photoionization yield was measured as a function of the detuning $\delta$ of the two-photon-resonant laser for several values of the intensity of the nonresonant laser. Typical experimental results are shown in Figs. 1 and 2.

In Fig. 3, we have plotted as a function of $I_{NR}$ the photoionization signal maximized with respect to the detuning $\delta$, for several different values of $I_R$. For low nonresonant-laser intensity, the photoionization yield is seen to increase with laser intensity; but at higher nonresonant-laser intensities, the yield decreases with increasing laser intensity. The dominant effect giving

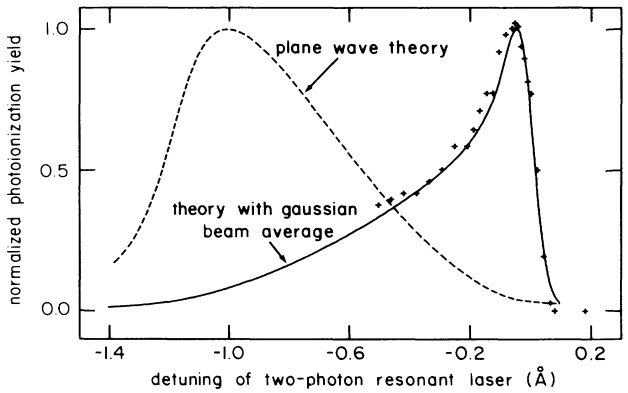


FIG. 1. Comparison of theoretical and experimental excitation spectra, for $I_{NR}=4.2$ GW cm$^{-2}$ and $I_R=6.4$ MW cm$^{-2}$. Excellent agreement is obtained only when the effects of the spatial distribution of intensity of the focused Gaussian laser beam are incorporated into the theory.

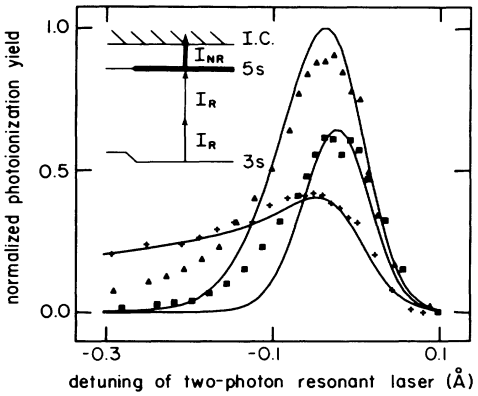


FIG. 2. Excitation spectra for several nonresonant laser intensities: pluses, 4.2 GW cm$^{-2}$; triangles, 0.42 GW cm$^{-2}$; squares, 0.067 GW cm$^{-2}$. The inset shows the relevant atomic energy levels and laser fields. The ground state is Stark shifted and the intermediate level is broadened as a result of both two-photon absorption and excitation to the ionization continuum (I.C.).

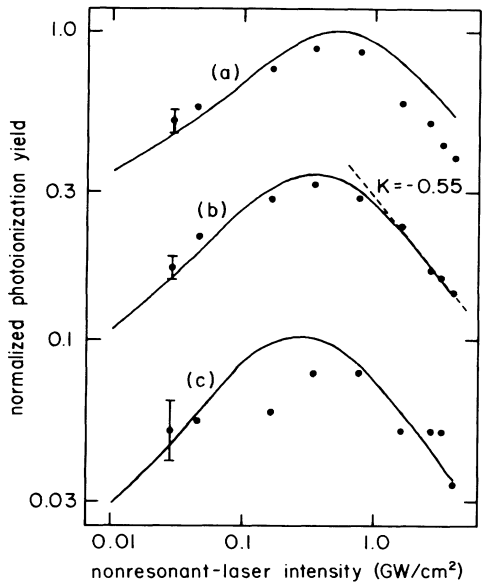


FIG. 3. Ionization yield vs the peak intensity of the nonresonant laser. Note the negative slope at high intensities. Each curve corresponds to a different intensity of the two-photon resonant laser: *a*, 13 MW cm$^{-2}$; *b*, 6.4 MW cm$^{-2}$; *c*, 3.2 MW cm$^{-2}$.

rise to the negative differential photoionization yield in this experiment is the nonresonant Stark shift, which in our experiment is much greater than the lifetime broadening. In photoionization experiments performed with an atomic beam,[6,7] the effect of nonresonant Stark shifts can be eliminated by retuning of the resonant laser. What is at first sight surprising is that in our experiment a negative differential yield was observed even when the resonant laser was retuned.

The basic processes involved in our experiment may be described[8] by an optical Bloch equation formalism[9] which takes account of the shift, the broadening, and the degree of excitation or saturation of the resonantly excited state. It is found that

$$\dot{u} = -[\delta - \Delta(t)]v - \kappa(t)u, \tag{1a}$$

$$\dot{v} = [\delta - \Delta(t)]u + \Omega_R(t)w - \kappa(t)v, \tag{1b}$$

$$\dot{w} = -\kappa(t)(r+w) - \Omega_R(t)v, \tag{1c}$$

$$\dot{r} = -\kappa(t)(r+w), \tag{1d}$$

where $u$ and $v$ are the in-phase and in-quadrature components of the two-photon Bloch vector; $w$ is the population difference between final and initial bound states; $r(t)$ is the total bound-state population; $\Omega_R(t)$ is the two-photon Rabi frequency, which for the transition of interest is given[9] by $1028 I_R$ rad sec$^{-1}$; $\Delta(t)$ is the Stark shift of the two-photon resonance given[9] by $-577(I_{NR}+10I_R)$ rad sec$^{-1}$; $\delta$ is the detuning from two-photon resonance; and $2\kappa(t)$ is the ionization rate given by $\sigma\Phi(t)$ where $\Phi(t)$ is the photon flux and $\sigma$ is the ionization cross section. The resonant ($I_R$) and nonresonant ($I_{NR}$) laser intensities are to be expressed in gigawatts per square centimeter. The cross section is taken to be $3.2\times10^{-17}$ cm$^2$, from which we obtain $\kappa = 56(I_{NR}+0.85I_R)$ sec$^{-1}$. The ion yield is given by $Y(t) = 1 - r(t)$. For square-pulse excitation these equations can be solved[8] for $r(t)$ to give

$$r(t) = [c_+ e^{-a_+ t} + c_- e^{a_+ t} + c_1 \cos a_- t + c_2 \sin a_- t]e^{-\kappa t}, \tag{2a}$$

where

$$c_\pm = \tfrac{1}{2}(a^2+b^2)^{-1}[(\kappa^2+b^2) \pm (\kappa/a)(\kappa^2+b^2-\Omega^2)], \tag{2b}$$

$$c_1 = (a^2-\kappa^2)/(a^2+b^2), \tag{2c}$$

$$c_2 = \kappa(a^2-\kappa^2+\Omega^2)/b(a^2+b^2), \tag{2d}$$

$$a_\pm = \{\pm\tfrac{1}{2}[\kappa^2-\Omega^2-(\delta-\Delta)^2] + \tfrac{1}{2}[(\kappa^2-\Omega^2-(\delta-\Delta)^2)^2 + 4(\delta-\Delta)^2\kappa^2]^{1/2}\}^{1/2}. \tag{2d}$$

These solutions can be adapted to meet the actual conditions of our experiment, including the time evolution of the laser pulse and the spatial distribution of laser intensity due to focusing. We model the temporal effects by decomposing the actual laser pulse into a sequence of twenty incremental square steps. We find that finer subdividision of the pulse does not lead to appreciably different predictions. These solutions, which still do not include the effects of focusing, predict an excitation spectrum shifted from zero detuning by $\sim 1$ Å, and a skewness in the opposite sense to that observed (see dashed curve in Fig. 1). To obtain complete agreement between theory and experiment, it is necessary to take account of the focusing of the Gaussian laser beam. Using the standard formula for the intensity distribution of a Gaussian beam, we calculate the volume element within the vapor cell that experiences each particular value of the laser intensity at the peak of the pulse. We then integrate the predicted yield per atom, which depends on the laser intensity, over the volume of the cell to obtain the final theoretical prediction.

In our experiment, the field at the focus is so intense that even at distances from the focus much greater than the confocal parameter the fields are sufficiently large to contribute significantly to the observed signal. The atoms far from the focus experience smaller Stark shifts than those at the focus. Thus the shift seen in the total signal is very much reduced from that experienced by the atoms in the strongest field. Moreover, the atoms near the focus are ionized by the leading edge of the pulse, well before they experience the maximum possible Stark shift. Each of these effects leads toward a resultant spectrum which peaks near zero, and which shades only to negative detunings. The resultant distribution becomes that seen as the solid curve in Fig. 1, which is in very good agreement with our data. In Fig. 2, we see a series of curves for the excitation spectrum for a number of nonresonant laser intensities. In each case the agreement between theory and experiment is very good. For all these curves the same value of the photoionization cross section and the ion collection efficiency has been used; there are no other free parameters.

The allowance for the focusing effect also produces excellent agreement between theory and experiment for the photoionization yield versus nonresonant laser intensity (see Fig. 3). Even though the resonant laser was retuned at each intensity of the nonresonant laser to give maximum signal, the curves still have a negative slope at high intensities. Hence, there exists a value of the laser intensity that maximizes the photoionization yield. This shows that optimization of resonant photoionization experiments is more subtle than previously appreciated.

Experimental data for an atomic multiphoton process are commonly expressed in terms of an exponential index,[10] which for our two-laser experiment we generalize as $K = \partial(\log Y)/\partial(\log I_{NR})$. At low laser intensities, the dependence of the photoionization yield is that of perturbation theory: The rate of ion production scales as $I_R^2 I_{NR}$ and thus $K$ as defined above is equal to $+1$. At sufficiently high nonresonant laser intensities, every atom excited to the two-photon-resonant level is rapidly ionized, and hence contributes to the photoionization signal. However, the Stark shift of the ground state induced by the intense nonresonant laser field shifts the atomic resonance away from the frequency of the other laser, leading to a decreased rate of two-photon absorption. The rate of ion production thus scales as $I_R^2/I_{NR}$ and the slope $K$ of the yield curve becomes $-1$. We observe a value of $K = -0.55$. This value is an average of the positive and negative values of $K$ appropriate to the range of intensities distributed throughout the volume of the cell. Negative $K$ has been discussed and analyzed[10,11] previously, but only one example has been observed.[6] This observation was in an atomic beam experiment, where simply retuning the resonant laser in order to reacquire the atomic resonance would have eliminated the effect. In our experiment in a cell, retuning the resonant laser does not eliminate the effect, because different atoms experience different intensities and hence different Stark shifts due to the focusing effect. Negative $K$ thus persists for any laser detuning.

Ackerhalt and Eberly[12] have shown that in order to maximize the photoionization yield in a multistep photoionization process, it is generally desirable to choose the laser intensities and detunings such that each step in the process occurs at a rate larger than that of the preceding. Our results confirm their predictions for low and intermediate intensities. However, at high laser intensities the nonresonant ac Stark effect, which was not included in their analysis, dominates the dynamics, leading to the negative differential yield observed in our experiment.

The excellent agreement between theory and experiment shown in Figs. 2 and 3 required the use of a photoionization cross section for the sodium $5s$ level of $3.2\times10^{-17}$ cm$^2$. If a value differing from this by as little as a factor of 2 is used, it is impossible to obtain even qualitative agreement between theory and experiment. This value is $\sim 20$ times larger than the theoretical value of Aymar,[13] which is in good agreement with the experimental value $1.5\times10^{-18}$ cm$^2$ measured by Smith *et al.*[4] However, their experiment was performed in an atomic beam with laser intensities of the order of 1 MW cm$^{-2}$, whereas our nonresonant laser intensity was as large as 10 GW cm$^{-2}$. Above-threshold ionization is a process that can lead to new ionization channels,[14] leading to what is effectively an intensity-dependent cross section. The rate of above-

threshold ionization is known to increase rapidly with both laser intensity and atomic number density. In conclusion, the observation of a negative exponential index, $K$, at high laser intensities implies the existence of an optimum laser intensity to maximize the photoionization yield in experiments utilizing a tightly focused laser beam. The precise details of this process are accurately predicted by the two-photon Bloch equations when account is taken of the effects of focusing of the Gaussian laser beams.

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