Multiphoton π Pulses

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(Received 20 May 2002; published 9 December 2002)

Multiphoton excitation in a two-level system is exceedingly weak because of small multiphoton coupling strengths, large ac Stark shifts, and ionization. I will discuss a three-level system in which the ac Stark shift is greatly reduced and the multiphoton coupling strength is greatly enhanced over a two-level system, to such an extent that multiphoton π pulses can be produced. I will also present two-electron calculations in a model potential, including ionization that shows a 12-photon π pulse driven with 800-nm photons. This three-level configuration may provide the basis for an amplifying medium in the vacuum ultraviolet, as well as multiphoton adiabatic passage and innershell ionization.

DOI: 10.1103/PhysRevLett.89.263001 PACS numbers: 33.80.Rv, 33.80.–b, 32.80.Rm, 42.50.Hz

Single photon absorption by atoms, molecules, or solids is an interaction of fundamental importance in many areas of physics. Recent applications include cooling and trapping of atoms [1], adiabatic population transfer [2], electromagnetically induced transparence [3], and slowing and stopping of light [4], to name just a few.

At high laser intensities, multiphoton processes become possible [5], and there was hope early on that processes generally associated with single photons could be driven through multiphoton interactions, in particular, the population of highly excited states of atoms and molecules [6,7]. Unfortunately, it was quickly shown that, within a two-level model, multiphoton excitation rates are exceedingly small and that ionization will generally dominate the interaction [8]. The main problem is that the high laser intensities required to overcome the weak multiphoton coupling strength also produce large ac Stark shifts. These Stark shifts move the energy levels of the material in a complex way making it impossible to maintain a multiphoton resonance for an appreciable time during the laser pulse. Not surprisingly, at intensities above 10^{11} W/cm^2, nearly all the work on the interaction of intense laser pulses with matter has focused almost exclusively on other processes, such as high-harmonic generation [9] and ionization [10]. Experiments designed to measure the excitation of atoms by strong laser fields have shown that less than 1% of the population is left in excited states and is distributed over a large number of Rydberg states [11]. Nevertheless, the usefulness of multiphoton excitation for a variety of experiments has recently been reviewed [12] and, it turns out, the results of the two-level calculations were unduly pessimistic.

In this Letter, I will analyze a three-level system that avoids the fundamental limitations found in the two-level system. Rather than coupling the ground state to a single excited state, I will replace the excited state with a pair of degenerate (or nearly degenerate) levels that have a strong dipole coupling. When driven by an intense laser, these strongly coupled levels produce a ladder of Floquet states [13]. The remarkable features of this ladder are that, unlike the two-level system, it has *no* ac Stark shift and both even and odd orders are present. The ground state couples to this ladder through a weak one-photon transition that produces only a small Stark shift. As a result, multiphoton excitation rates are so strong that π pulses can easily be driven.

Although this model three-level system works exceptionally well, it is important to ask whether it has any physical realization. The answer to this is emphatically "yes": all evenly charged homonuclear diatomic molecular ions have this level structure [14]. Indeed, this molecular configuration has, for many years, been the one outstanding example of efficient multiphoton excitation [15–18], although, until now, there had been no explanation for this strong excitation.

Finally, to truly establish the feasibility of this approach to multiphoton excitation, I will present fully correlated two-electron calculations in a 1D model molecular potential, including ionization, to show that a single state 18.6 eV above the ground state can be populated with high efficiency ($>90\%$) and little ionization with a short 800-nm laser pulse. Moreover, the ground state is completely depopulated. Overall, this corresponds to a 12-photon π pulse.

The three-level system (see Fig. 1) of interest here can be represented by the following time dependent Hamiltonian:

$$H(t) = \begin{bmatrix} E_1 & \Omega_{12}(t) & 0 \\ \Omega_{12}(t) & 0 & \Omega_{23}(t) \\ 0 & \Omega_{23}(t) & 0 \end{bmatrix}, \qquad (1)$$

where E_1 is the energy of level one and $\Omega_{ij}(t) = R_{ij}F_o f(t)\cos(\omega t)$. R_{12} and R_{23} are the dipole matrix elements between levels one and two and levels two and three, respectively. F_o is the peak field strength, $f(t)$ is a normalized pulse envelope, and ω is the laser frequency. All quantities are in atomic units, throughout this Letter. Since levels two and three are interchangeable, it does not matter which is coupled to level one. There are two

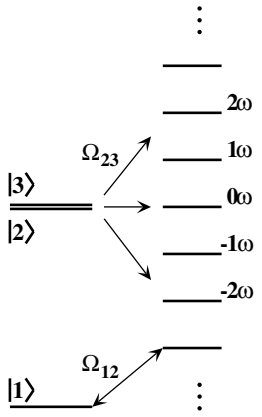

FIG. 1. Couplings in the three-level system showing the Floquet ladder of states produced by the upper states along with the one-photon transition to the ground state.

important assumptions: $R_{23} \gg R_{12}$ and $|E_1| \gg \omega$. If the amplitudes of the populations of the three levels are c_1, c_2, and c_3, then they satisfy the following equations:

$$i\dot{c_1} = E_1 c_1 + \Omega_{12} c_2, \qquad i\dot{c_2} = \Omega_{12} c_1 + \Omega_{23} c_3, \qquad i\dot{c_3} = \Omega_{23} c_2. \tag{2}$$

To interpret this set of equations, consider just the coupling between the upper levels: $i\dot{c_2} = \Omega_{23} c_3$ and $i\dot{c_3} = \Omega_{23} c_2$. These equations can be solved by first finding $c_+ = c_2 + c_3$ and $c_- = c_2 - c_3$ and converting back to c_1 and c_2. The result is the following:

$$c_2 = \cos[\phi(t)], \qquad c_3 = -i \sin[\phi(t)], \tag{3}$$

where $\phi(t) = \int_{t_0}^{t} \Omega_{23}(t')dt'$ and the initial conditions are specified at t_0. The key feature is that the modulation is *linear* in the field, as are the eigenvalues, $\pm\Omega_{23}$, making the time average of the eigenvalues zero. This leads to a vanishing ac Stark shift. The combined Fourier spectrum of c_2 and c_3 consists of peaks centered exactly at $\pm n\omega$, where n is any positive integer, and with amplitudes given by Bessel functions of order n, J_n. This series of peaks corresponds to the Floquet ladder of states shown in Fig. 1. Level one couples to the $-(n-1)\omega$ Floquet state through Ω_{12}. This one-photon coupling to the Floquet state can be solved for exactly [19], giving the n-photon Rabi frequency out of level one, for constant field strength, F_o, at the n-photon resonance, $n\omega = |E_1|$:

$$\Omega_n^{(\text{three-level})}(F_o) = 2n\omega \left(\frac{R_{12}}{R_{23}}\right) J_n\left(\frac{R_{23}F_o}{\omega}\right). \tag{4}$$

In the perturbative limit, $R_{23}F_o \ll \omega$,

$$\Omega_n^{(\text{three-level})}(F_o) = \frac{2\omega}{(n-1)!}\left(\frac{R_{12}}{R_{23}}\right)\left(\frac{R_{23}F_o}{2\omega}\right)^n. \tag{5}$$

For comparison, the two-level system has been extensively studied [8,13], and a particularly simple expression for the corresponding n-photon Rabi frequency is [8]:

$$\Omega_n^{(\text{two-level})}(F_o) = \frac{2\omega}{\pi}\left(\frac{eR_{12}F_o}{2n\omega}\right)^n, \tag{6}$$

where $e = 2.7183$. The ac Stark shift in the two-level system is quadratic in the field, Ω_{12}^2/E_1, and does not have a zero time average.

To quantitatively demonstrate the advantages of the three-level system, I determined the photon frequency and field strength required for complete population transfer using a multiphoton transition with and without the coupling between the upper two levels for two different pulse shapes (see Table I). The values of R_{12} and R_{23} were chosen to correspond to the molecular model discussed below.

In these data, the differences between the two- and three-level systems are quite evident. Equations (4) and (6) were obtained for constant field strength and should be compared to the results for the square pulse calculation. For the three-level case, Eq. (4) agrees well with the calculations. The required laser frequency is not quite equal to the field-free n-photon resonance because of the small ac Stark shift. For the Gaussian pulse shape with the same n-photon pulse area, the results are virtually identical to the square pulse.

The results for the two-level system are dramatically different. First, Eq. (6) is not so accurate, as it includes many approximations, but, more importantly, the

TABLE I. Laser frequency and field strength required for an n-order π pulse for the two-level and three-level systems. The analytic result for the required field strength for the square pulse comes from setting $\Omega_n(F_o)T_n = \pi$, with $T_7 = 350$ and $T_9 = 390$. The calculated values come from directly integrating Eq. (2), where $E_1 = -1.0$, $R_{12} = 0.5$, and $R_{23} = 0$ (two-level) or 3.0 (three-level). For the Gaussian pulse, $\exp(-t^2/\tau^2)$, $\tau = \sqrt{n/\pi}T_n$.

			Two-level				Three-level			
Photon order, n	Field-free frequency	Pulse shape	Analytic field	Calculation Field	Calculation Frequency	Calculation Stark shift	Analytic field	Calculation Field	Calculation Frequency	Calculation Stark shift
7	0.1429	Square	1.0575	1.3868	0.1980	0.3860	0.2105	0.2175	0.1449	0.0143
		Gaussian		1.5882	0.2107	0.4749		0.2147	0.1446	0.0122
9	0.1111	Square	1.1644	1.7313	0.1721	0.5489	0.2266	0.2371	0.1131	0.0179
		Gaussian		2.1591	0.1879	0.6911		0.2337	0.1128	0.0152

required field strengths and corresponding Stark shifts are much larger than in the three-level system. Second, because of the large Stark shifts, even higher field strengths are needed for the Gaussian pulse shape, as it is impossible to maintain the n-photon resonance during the entire pulse. Finally, although it is always possible to find conditions in the two-level system producing a π pulse, the results are somewhat artificial: At these high field strengths, ionization will certainly set in. All of these observations of the two-level system are in agreement with Ref. 8].

Although this three-level system clearly shows that high order multiphoton processes can be driven much more efficiently than in the two-level system, this scheme must be tested in a real physical system. As mentioned above, there has been little evidence of the direct multiphoton population transfer to excited states except for one experiment that has consistently implied such excitation: the simple observation of the charge asymmetric dissociation of diatomic molecules ionized by strong laser fields [15,17,18,20]. For example, the dissociation of N_2^{4+} into $N^{3+} + N^{1+}$ means that the original N_2^{4+} molecule must be in an excited state, otherwise it would dissociate into $N^{2+} + N^{2+}$ [20]. The degree of excitation can be estimated from the known atomic ionization potentials and is about 18.6 eV. Furthermore, the efficiency of the excitation can be estimated from the relative abundance of the two channels and it has been observed that the asymmetric channels are in the range of 10%–30% for ultrashort (~ 30 fs) laser pulses [18]. Moreover, this effect is quite robust as asymmetric dissociation has been observed up to $I_2^{12+} \rightarrow I^{7+} + I^{5+}$ [18]. Motivated by these findings, I chose a Hamiltonian corresponding to two electrons in a double well potential. The one-dimensional form of this can be written as the sum of a spatial term, H_s, and a momentum term, H_p: $H(t) = H_s(t) + H_p(t)$, where $H_p(p_1, p_2, t) = p_1^2/2 + p_2^2/2$ and

$$H_s(x_1, x_2, t) = \frac{-Z}{\sqrt{(x_1 - d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_1 + d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_2 - d)^2 + a^2}} + \frac{-Z}{\sqrt{(x_2 + d)^2 + a^2}} + \frac{1}{\sqrt{(x_1 - x_2)^2 + a^2}} + (x_1 + x_2)F(t). \tag{7}$$

$D = 2d$ is the internuclear separation, $F(t)$ is the field strength, a is a smoothing parameter, Z is the charge on each atom, and x_1, x_2 (p_1, p_2) are the positions (momenta) of the electrons. This 1D "soft Coulomb" potential has been widely used to study strong field interactions with both two-electron atoms [21] and molecules [22]. To ensure that the results were not dependent on the representation of the interaction, a direct comparison was made for a few cases between the length form, Fx, and momentum form, Ap (where A is the vector potential). The populations of the various levels agreed to better than 1%. The ground state wave function is found by integrating in imaginary time. Excited states are found the same way, except that all lower lying states are projected out on each time step. The symmetry of the wave function depends on whether one is considering singlet or triplet states. In all that follows, the singlet states are used. Figure 2 shows the five lowest energy levels of this Hamiltonian as a function of internuclear separation, D, for $Z = 3$ and $a = 0.742$, which roughly corresponds to N_2^{4+}. As can be seen in the figure, there is a large energy gap between the ground and first excited states. Moreover, the first excited states are actually a pair of nearly degenerate states with opposite parity and, hence, are strongly coupled. Indeed, at an internuclear separation of 3.5, the couplings between these three states are $R_{12} = 0.50$, $R_{23} = 3.0$. Thus, the conditions are met for having a strong multiphoton coupling between them. There is also a clear connection to the experimental observations mentioned above: The ground state correlates with charge symmetric dissociation while the first pair of excited states correlate with charge asymmetric dissociation. The importance of the excited state pair has recently been discussed in Refs. [22,23]. To calculate the time behavior of this system, the wave function is followed on a 135×135 spatial grid with a step size of 0.15. The spatial part of the Hamiltonian is applied as $\exp(-iH_s\Delta t)$ with a time step of $\Delta t = 0.1$. The wave function is then transformed into momentum space, where the momentum Hamiltonian $\exp(-iH_p\Delta t)$ is applied and transformed back to real space. Finally, an absorbing border is placed around the edge of the spatial grid to prevent reflections and allow for ionization.

The main result of the calculations is the population of the three lowest lying levels at the end of the Gaussian laser pulse as a function of internuclear separation, shown in Fig. 3. The laser frequency was held constant at a value corresponding to 800 nm radiation and the field at 0.215 a.u. with a pulse duration of 244 a.u. Therefore,

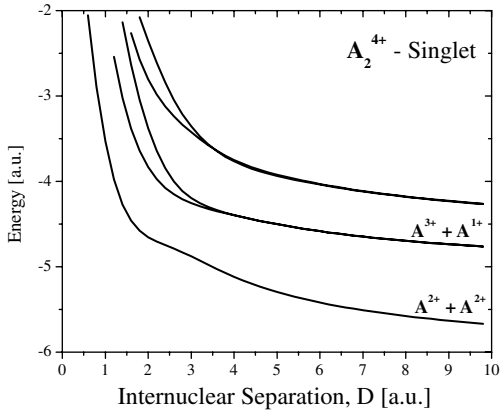

FIG. 2. Potential energy curves for the model molecule A_2^{4+}, including the internuclear repulsion, Z^2/D.

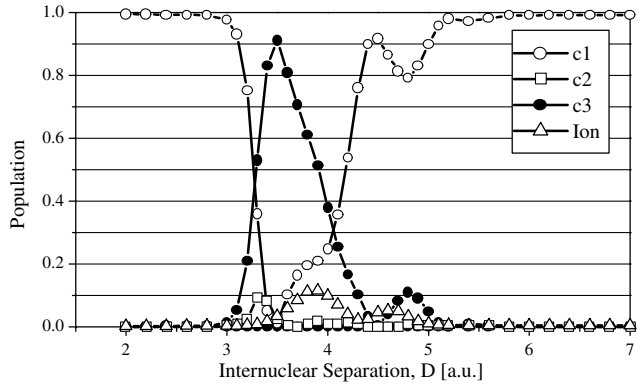

FIG. 3. Population of the three lowest lying levels as well as ionization as a function of internuclear separation for the 1D model molecule.

the laser is unlikely to be resonant with any particular transition. However, because of the shape of the potential energy curves, the energy difference between the ground and first pair of excited states varies as a function of internuclear separation and so there will always be values of D where the laser comes into resonance. The field-free 12-photon resonance, which, by symmetry, couples the ground state with the gerade excited state, occurs at $D = 3.5$ a.u. and accounts for the major feature in the data. The maximum excitation rate also occurs at this separation, even in the presence of the field because of the dramatically reduced ac Stark shift. As can be seen, the excited state population goes above 90%, the ground state is almost completely emptied, and the ionized fraction is less than 5%. Thus, in a full quantum system with an infinite number of bound states and a continuum, this particular three-level structure still allows for a high degree of excitation of a particular state through a multiphoton resonance. Furthermore, in this system, the upper states are not perfectly degenerate showing that degeneracy is not an exact requirement.

A real system, such as N_2^{4+}, will be yet more complex than the $2e$ calculations. Here again, the reduced field strength and ac Stark shift is highly advantageous. Extraneous states are less likely to be coupled to, as they will generally be nonresonant and they, themselves, will produce less of a Stark shift of the states of interest. Nevertheless, if other states do have a strong coupling to the upper states of the three-level system and contribute to a large ac Stark shift, then the π pulse will fail. This may limit the usefulness of this approach in atoms. However, additional states also raise a different possibility—the strongly coupled pair of levels can be the lower levels of a three-level system, as well. Once the molecule has been excited from the ground state to the pair of excited states, as the molecule continues to dissociate, this pair may come into resonance with an even higher state. At this point, there will be a strong coupling with this state, further exciting the molecule. This may explain the observation that the fragment ions following charge asymmetric dissociation can themselves be in an excited state [24].

I acknowledge useful conversations with G. Dunne, R. Jones, and J. Javanainen, as well as support from the NSF under Grant No. NSF-PHYS-9987804.

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