Two-color ionization of hydrogen for frequencies in the 2:3 ratio

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We present Floquet calculations of the total rate for multiphoton ionization of atomic hydrogen by a coherent superposition of the second and third harmonics of a Nd:YLF (neodymium-doped yttrium-lithium-fluoride) laser field. The total rate depends little on the relative phase of the two fields in the range of intensity considered.

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Accurate nonperturbative calculations of the rate for ionization of atomic hydrogen by bichromatic optical fields have become possible in recent years. In particular, several sets of results have been reported, for the interesting case where the atom decays under the joint effect of two intense laser fields with commensurable frequencies and a constant relative phase. Schafer and Kulander [1,2] have presented time-dependent calculations for a superposition of an intense field and its second, double-frequency harmonic, for a few pairs of wavelengths. Their study was motivated by a recent experiment in krypton [3], and focused on the dependence of the ionization rates, angular distributions, and above-threshold ionization (ATI) spectra on the relative phase of the two fields. Detailed calculations of total ionization rates in the (time-independent) Floquet approach have also been reported, for hydrogen atoms exposed to an intense 616-nm field and its second or third harmonic as well as for a few other fundamental wavelengths and for frequencies in the 1:5 or 1:7 ratio [4,5]. Two-color coherent processes in weak fields have received more attention, both in experiment and in theory, mainly in relation to the study of harmonic generation and of phase control of reactions [6]. Nonperturbative calculations in He [7] and recently in H_2^+ [8] have also been reported, as well as studies of laser-assisted potential scattering [9] and of microwave ionization [10].

In this work we extend the Floquet calculations of Refs. [4] and [5] to the case where the atom is irradiated simultaneously by the second and third harmonics of the same laser field, since this case, too, is of current experimental interest. The method can be sketched as follows [11]. We assume that the intensity can be considered as being constant during the ionization process, make the dipole approximation, and write the total electric field vector as

$$\boldsymbol{F}(t) = \boldsymbol{F}_2 \cos(2\omega t) + \boldsymbol{F}_3 \cos(3\omega t + \phi). \tag{1}$$

Here $\omega = 0.04325$ a.u. is the fundamental angular frequency of the Nd:YLF (neodymium-doped yttrium-lithium-flouride) laser (1053-nm wavelength). (Interesting effects may arise from the finite bandwidth of the laser fields, which we do not take into account, although it is unlikely that these effects would amplify the very weak dependence on ϕ of the total ionization rate that is found when the bandwidth is neglected.) The perfect periodicity of $\boldsymbol{F}(t)$ makes it possible to describe the decaying atom by a state vector of the form

$$|\Psi(t)\rangle = e^{-iEt/\hbar} \sum_N e^{-iN\omega t} |\mathcal{F}_N\rangle. \tag{2}$$

Thus $|\Psi(t)\rangle$ is a solution of the time-dependent Schrödinger equation for the Hamiltonian $H_a + V(t)$, where H_a is the Hamiltonian of the bare atom. The harmonic components $|\mathcal{F}_N\rangle$ satisfy the eigensystem

$$\begin{aligned}(E + N\hbar\omega - H_a)|\mathcal{F}_N\rangle &= V_{+2}|\mathcal{F}_{N-2}\rangle + V_{-2}|\mathcal{F}_{N+2}\rangle \\ &\quad + V_{+3}e^{-i\phi}|\mathcal{F}_{N-3}\rangle + V_{-3}e^{i\phi}|\mathcal{F}_{N+3}\rangle\end{aligned} \tag{3}$$

and Siegert boundary conditions in the gauge where

$$V(t) = -(e/\mu c)[\boldsymbol{A}_2 \sin(2\omega t) + \boldsymbol{A}_3 \sin(3\omega t + \phi)] \cdot \boldsymbol{p} \tag{4a}$$

$$\equiv V_{+2}e^{-2i\omega t} + V_{-2}e^{2i\omega t} + V_{+3}e^{-3i\omega t - i\phi} + V_{-3}e^{3i\omega t + i\phi}, \tag{4b}$$

with μ the electron mass. The total ionization rate from the dressed $1s$ state is $-2\,\mathrm{Im}(E)/\hbar$ if $|\Psi(t)\rangle$ is the Floquet state vector that reduces to the bare $1s$ state vector in the zero-field limit. The eigensystem is solved numerically by expanding the harmonic components on a discrete basis set of spherical harmonics and complex radial Sturmian functions. We consider only the case where both fields are linearly polarized along the same direction; this restriction eases the burden of calculation appreciably, since the initial state is then coupled only to states with the same cylindrical symmetry with respect to that direction.

The total ionization rate is a periodic function of the relative phase of the two harmonics, ϕ. The period of this function is $\pi/2$ for frequencies in the 2:3 ratio. Indeed, any two pathways to the continuum involving absorption of different numbers of third harmonic photons cannot add coherently in the *total* rate (integrated over angles) unless these numbers differ by an integral multiple of 4, for it is only in this case that the pathways may lead to the same continuum state. Whence the total rate depends on ϕ only through integral powers of $\exp(4i\phi)$, which implies the $\pi/2$ period. The period can also be de-

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duced from the symmetry of the problem [1–3]: adding $\pi/2$ to ϕ in $F(t)$ can be offset by a shift of the origin of time of $-\pi/(2\omega)$ and a reversal of the direction of polarization which do not affect the total rate. In addition to being a periodic function, the total rate is also an even function of the relative phase [4,5]; thus its value for a relative phase ϕ is the same as that for the relative phases $\pm\pi/2 - \phi$, $\pm\pi/2 + \phi$, $\pi \pm \phi$, and $-\phi$.

When both harmonic fields are weak, the atom cannot decay by absorbing less than six photons of energy $2\hbar\omega$, or four photons of frequency $3\hbar\omega$, or three photons of frequency $2\hbar\omega$ and two photons of frequency $3\hbar\omega$. Therefore the slowest photoelectrons are ejected with an energy $\mathrm{Re}(E) + 12\hbar\omega$. Because of the ac Stark shift, this channel closes when $I_2 + 4/9 I_3$ is about 2.0×10^{13} W/cm^2, with I_2 and I_3 denoting, respectively, the intensity of the second harmonic and the intensity of the third harmonic. (The Stark shift is essentially the sum of the ponderomotive shift of each field acting separately, hence the 4/9 factor.) The intensity where the threshold is crossed varies rapidly with ω; for example, the threshold is crossed at about 1.4×10^{13} W/cm^2 instead of about 2.0×10^{13} W/cm^2 when the fundamental wavelength is 1064 nm instead of 1053 nm.

The total ionization rate for varying I_2 and I_3 with a constant ratio I_2/I_3 is shown in Fig. 1, for intensities below the threshold intensity; resonances with intermediate Rydberg states make it difficult to perform accurate calculations between 2×10^{13} and about 4×10^{13} W/cm^2. The total ionization rate for varying I_3 and fixed $I_2 = 1 \times 10^{13}$ W/cm^2 is shown in Fig. 2(a). The results of Figs. 1 and 2(a) were obtained with $\phi = 0$. As long as the intensity of the low frequency field does not exceed about 1.5×10^{13} W/cm^2 the total ionization rate Γ remains small enough for depletion to be negligible for pulses of typical duration of the order of 1 ps; in these conditions, the total ionization probability for ionization by a short square pulse of duration τ is essentially $\Gamma\tau$.

As is the case for frequencies in the 1:2 or 1:3 ratio, the rate of ionization by the two fields superposed coherently is much larger than the arithmetic sum of the rates of ionization by each field acting independently. However, the increase in the rate when the fields act in synergy tends

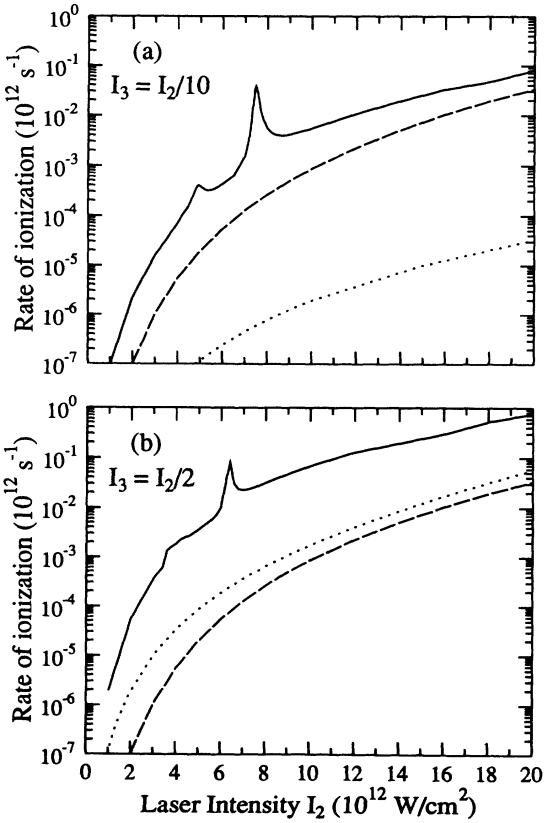

FIG. 1. Total ionization rate of H(1s) irradiated by a field of wavelength 526.5 nm and intensity I_2 and a field of wavelength 351 nm and intensity $I_3 = I_2/10$ (a) or $I_2/2$ (b), with $\phi = 0$. Dashed line: $I_3 = 0$ (second harmonic acting alone). Dotted lines: rate for ionization by the third harmonic acting alone with an intensity which is either 1/10 (a) or 1/2 (b) the intensity shown on the lower scale.

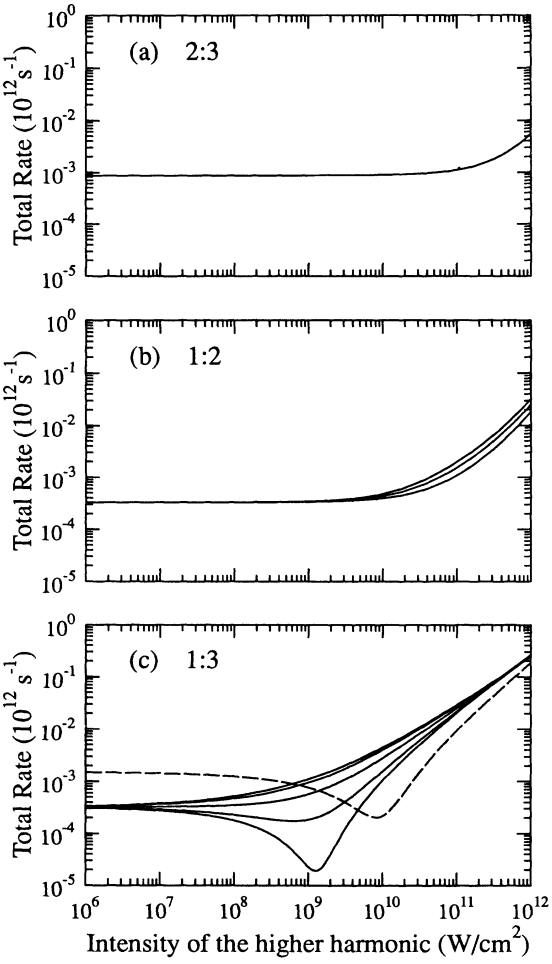

FIG. 2. (a) Total ionization rate of H(1s) irradiated by a field of wavelength 526.5 nm and intensity 1.0×10^{13} W/cm^2 and a field of wavelength 351 nm, vs the intensity of the latter; $\phi = 0$. (b) Rate for a superposition of a field of wavelength 616 nm and intensity $I_1 = 1.0 \times 10^{13}$ W/cm^2 and its second harmonic, vs the intensity of the latter; from top to bottom, $\phi = 0$, $\pi/4$, and $\pi/2$. (c) Same as (b) but for the third harmonic of the 616 nm field. From top to bottom, $\phi = 0$, $\pi/4$, $\pi/2$, $3\pi/4$, and π. Dashed line: rate when the fundamental wavelength is 596 nm and $I_1 = 1.5 \times 10^{13}$ W/cm^2 with $\phi = \pi$.

to be less here than for the superposition of a field and its third harmonic, to the extent that such a comparison can be made. Resonances with states belonging to the $n = 4$ manifold show up in the solid lines of Fig. 1, between 4 and 8×10^{12} W/cm^2, though there is no structure in the dotted and dashed lines. They occur when $\mathrm{Re}(E) + 11\hbar\omega \approx -1/32$ a.u., thus at lower values of I_2 for $I_3 = I_2/2$ than for $I_3 = I_2/10$. The dressed $1s$ state is coupled resonantly to the $n = 4$ states through absorption of either one photon of energy $2\hbar\omega$ and three photons of energy $3\hbar\omega$, or four photons of energy $2\hbar\omega$ and one photon of energy $3\hbar\omega$. Therefore resonance is possible with every state of this manifold when the two fields act together, but is not possible with any of them when they act separately. The five-photon coupling appears to be stronger than the four-photon coupling at these intensities; indeed, the analysis of the wave function of the dressed $1s$ state indicates that the peaks are due to resonance with the dressed $4p$ and $4f$ states — the $4f$ resonance being the one appearing at higher intensity. (In fact, the dressed $4s$ and $4d$ states are very close in energy to the dressed $4f$ and $4p$ states, respectively, and shift into resonance at nearly the same intensities.)

In the range of intensities covered in Figs. 1 and 2, the total rate decreases when the relative phase ϕ increases. However, the variation is quite small; it is in general less than 1%, except in a small region of intensities (discussed below) where it amounts to 4%. (This does not rule out that the *differential* rate may depend on the relative phase in a more significant way [1,4].) Calculations were also performed at higher intensity, in the region where the initial state is in resonance with the $n = 4$ states (i.e., for $I_2 + 4/9I_3 \approx 4.5 \times 10^{13}$ W/cm^2); there also the variation is less than 4%. For the sake of comparison, total ionization rates are shown in Figs. 2(b) and 2(c), calculated for a coherent superposition of a field and its second or third harmonic, respectively; in Figs. 2(b) and 2(c) the total electric field vector is

$$\boldsymbol{F}(t) = \boldsymbol{F}_1 \cos(\omega t) + \boldsymbol{F}_q \cos(q\omega t + \phi), \tag{5}$$

with $2\pi c/\omega = 616$ nm. Phase-dependent interferences affect the multiphoton ionization rate a great deal more in these cases, the effect being the largest in relative magnitude for the 1:3 frequency ratio when the harmonic field is rather weak [12].

We believe that there are two reasons to the small magnitude of the variations observed in the 2:3 case. First, a number of pathways to the continuum contribute incoherently to the *total* rate for the 2:3 ratio of frequencies.

TABLE I. Net numbers of harmonic photons the atom should absorb for the electron be ejected with an energy $\mathrm{Re}(E) + N\hbar\omega$. N_2: number of photons of energy $2\hbar\omega$; N_3: number of photons of energy $3\hbar\omega$; Π: parity of the continuum state.

	N_2	N_3	N	Π
(a)	6	0	12	+
(b)	3	2	12	−
(c)	0	4	12	+
(d)	5	1	13	+
(e)	2	3	13	−

(On this count, a stronger dependence in ϕ of the angular distributions can be expected since the pathways to states of the same final energy always contribute coherently to the *differential* rate.) Second, the possibility of a significant variation of the total rate is reduced further by the fact that its dependence on ϕ is entirely due to interferences between couplings with photon numbers differing by at least six second harmonic photons and four third harmonic photons. Such couplings differ considerably in their dependence on I_2 and I_3, which limits the range of intensity where their interference may affect the rate. For example, among the ionization amplitudes for the photon numbers listed in Table I, only those for the combinations (a) and (c) can contribute to the phase dependence of the total ionization rate of Figs. 1 and 2(a) since the other ones correspond to final states with different parity and/or energy. At $I_2 = 1 \times 10^{13}$ W/cm^2 these two amplitudes are close in absolute magnitude in a narrow interval of intensity around $I_3 = 6 \times 10^{12}$ W/cm^2, within which the variation of the total ionization rate with ϕ increases from less than 1% to about 4%.

In contrast to the 2:3 case, all pathways leading to continuum states of the same energy interfere in the 1:3 case. The scope for interference is also greater in the 1:2 case, although there is no interference in the total ionization rate between pathways involving an even number of second harmonic photons and those involving an odd number. The coexistence of uninterfering pathways in the 1:2 and 2:3 cases makes it more unlikely that the atom may become more stable against ionization when the harmonic field is turned on, contrary to what has been found in the 1:3 case.

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