Enhanced harmonic generation in extended molecular systems by two-color excitation

A. D. Bandrauk, S. Chelkowski, and H. Yu
Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

E. Constant
Centre de Physique Moleculaire Optique et Hertzienne, Université de Bordeaux I, 33405 Talence, France
(Received 9 June 1997)

Numerical simulations of high-order harmonic generation in the molecular ions H_2^+ and H_3^{2+} show that two-color intense ($I \simeq 10^{14}$ W/cm^2) short (<1-psec) laser pulse excitation produces harmonics at large internuclear distances with larger efficiencies (intensities) at $6U_p$, $8U_p$, and $10U_p$ energies than in single-atom single-frequency excitation. The two-color excitation scheme creates efficient high harmonics by first ionizing electrons with a high-frequency laser pulse and accelerating them with lower frequency towards neighboring atoms. Such two-color schemes should be useful for enhancing high-order harmonic generation in clusters. [S1050-2947(97)50310-6]

PACS number(s): 42.50.Hz, 42.65.Ky

Generation of high-order harmonics has been achieved recently in several laboratories with orders exceeding 100 by exciting rare-gas atoms with short (subpicosecond) intense ($I \geqslant 10^{14}$ W/cm^2) laser pulses [1,2]. Recent quasiclassical interpretations of such high-order harmonic generation (HG) rely on a simple classical model wherein the electron first tunnels from the ground state of the atom, through the barrier formed by the Coulomb potential and the laser field, and then is rescattered towards the ion by the changing phase of the intense electromagnetic field [3–6]. Thus after tunnelling out of the atom, the electron moves under the influence of an oscillating electric field and, neglecting Coulomb interactions, the equation of motion becomes (in a.u.)

$$\ddot{Z}(t) = E_0 \cos(\omega t + \varphi),$$

$$\dot{Z}(t) = (E_0/\omega)[\sin(\omega t + \varphi) - \sin(\varphi)],$$

$$Z(t) = (E_0/\omega^2)[\cos(\varphi) - \cos(\omega t + \varphi) - \omega t \sin(\varphi)], \quad (1)$$

with the initial condition $\dot{Z}(0) = Z(0) = 0$. A recollision between the ionized electron and its parent ion occurs whenever $Z(t) = 0$ or equivalently $\tan\varphi = (\cos\omega t - 1)/(\sin\omega t - \omega t)$. Maximizing the velocity $\dot{Z}(t)$ with the above phase condition gives the field-induced maximum kinetic energy in atomic units,

$$E_{\max} = |\dot{Z}|^2/2 = 3.17U_p, \quad U_p = E^2/4\omega^2, \quad (2)$$

i.e., $\ddot{Z}(t) = 0$ with the phase φ defined above. Thus high-order harmonic generation results in a well-defined cutoff at a maximum harmonic order $N_{\max}$,

$$N_{\max} = (I_p + 3.17U_p)/\hbar\omega, \quad (3)$$

where I_p is the ionization potential and U_p the ponderomotive energy.

High-order harmonic generation opens possibilities as a source of coherent radiation in the extreme region, and recent applications of such coherent sources are now in progress [7–9]. Thus there is interest in extending the limiting cutoff law (3) to higher order. Our previous exact calculations of HG in the molecular ion H_2^+ [10,11] have shown enhanced HG intensities at large critical distances R_c, where molecular ions tend toward charge-resonance-enhanced ionization (CREI). Thus for H_2^+, R_c is predicted to be $4/I_p = 8$ a.u. [12] and for H_3^{2+}, $R_c = 5/I_p = 10$ a.u. [13]. At these critical distances the molecular ions exhibit large ionization rates due to field-induced Coulomb-barrier suppression effects [12,14] and also electron localization [11]. These large ionization rates exceed those of the neutral atom by one or two orders of magnitude (see Fig. 1) thus leading to efficient high-order HG with intensities exceeding those of the atom by at least one order of magnitude [10]. Yet previous measurements of HG in molecular gases have shown results very similar to those obtained in atomic gases [15,16], i.e., the same cutoff law (3) was found to apply to molecular gases. The most obvious explanation is that HG occurs on a time scale much shorter than molecular dissociation, so that the distances R_c of enhanced ionization and enhanced HG are never reached,

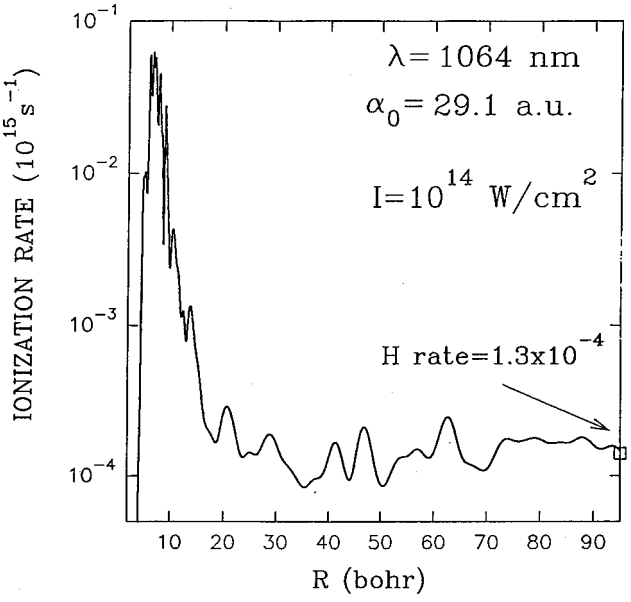

FIG. 1. Ionization rates of 1D H_2^+ for $\lambda = 1064$ nm, $I = 10^{14}$ W/cm^2 laser excitation as a function of internuclear distance R.

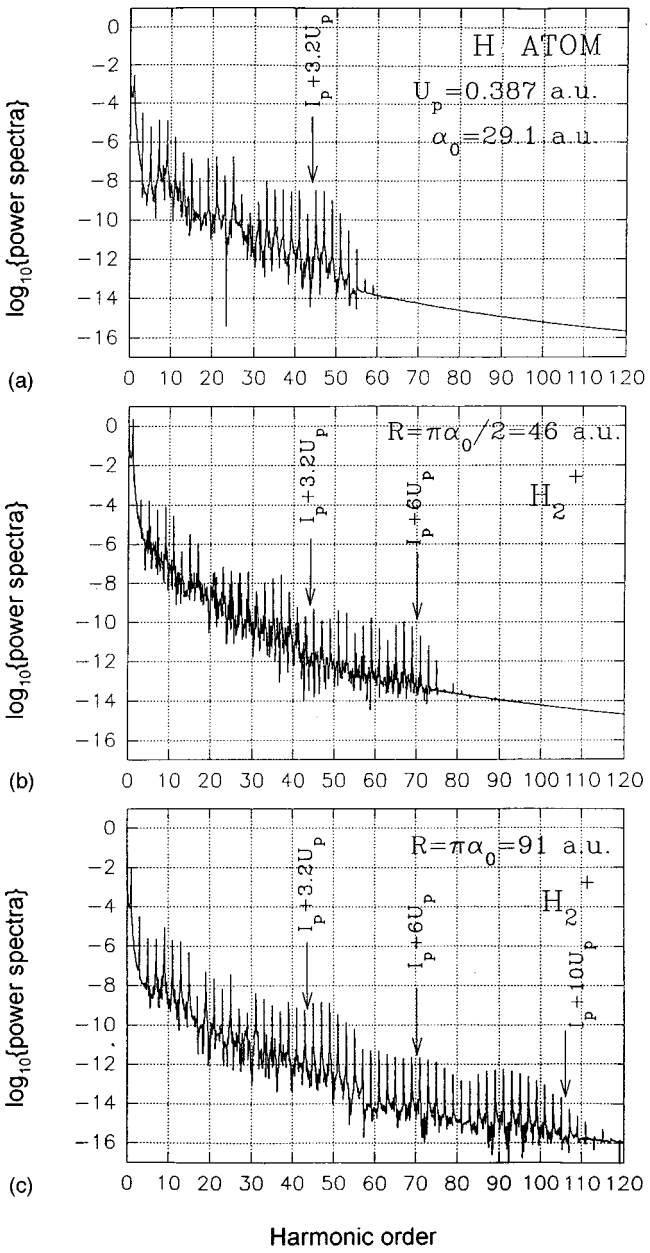

FIG. 2. Harmonic generation spectra for $\lambda=1064$ nm, $I=10^{14}$ W/cm^{23} laser excitation: (a) H atom; (b) H_2^+ at $R=46=\pi\alpha_0/2$ a.u.; (c) H_2^+ at $R=91=\pi\alpha_0$ a.u.

i.e., the molecules emit HG at their equilibrium distance.

Returning to Eq. (1), one observes that the velocity $\dot{Z}(t)$ is maximum whenever $\ddot{Z}(t)=0$, which occurs for $(\omega t+\phi)=(2n+1)\pi/2$. For this condition one obtains $\dot{Z}(t,\max)=\pm 2E_0/\omega$ and $E_{\max}=8U_p$ with the initial phase $|\phi|=\pi/2$. The resulting electron distance from the nucleus is $Z=\pi\alpha_0$ from Eq. (1), where $\alpha_0=E/\omega^2$ is the ponderomotive radius. Such maximum kinetic energies of $8U_p$ have been previously predicted theoretically to occur in atomic above threshold ionization (ATI) spectra, but have been shown to be of negligible intensity [17] as they correspond to minima of the usual Bessel functions of multiphoton ATI theories [18]. In previous unpublished calculations of HG in H_2^+ we had observed $6U_p$ and $8U_p$ maxima in HG (see Fig. 2) at large internuclear distance $R>\alpha_0$, but these were of uninteresting low intensities. The source of this low-intensity HG can be obtained by perusal of Eq. (1): $8U_p$ energies are obtained for $Z=\pi\alpha_0$ when the initial field $E(t=0)=0$, since $|\phi|=\pi/2$. Thus not enough electrons are produced at $t=0$ to be accelerated later by half cycles ($\omega t=n\pi$), towards neighboring atoms. Recently Moreno *et al.* have suggested that energies higher than $8U_p$ can be obtained at large distances in molecules, provided the initial velocity $\dot{Z}(0)\neq 0$, and this should occur in the multiphoton ionization regime [19]. As pointed out above, the critical problem in obtaining efficient high-order HG beyond the $3U_p$ cutoff law (1) is usually the low ionization rates of electrons.

In the present paper we show that the combination of two laser fields can result in high-order HG producing harmonic energies up to $10U_p$. Thus the field combination

$$E(t)=E_0[\cos\omega t+0.5\cos(3\omega t+\phi)], \tag{4}$$

used before by us to control electron localization [20], produces the desired effect, with ϕ being the phase difference between the two fields. Previous two-color experiments have been reported for ionization and HG in atoms only [21,22]. The basic physics is that the high-frequency field 3ω ionizes the electrons initially with little ponderomotive energy $[U_p(3\omega)\ll U_p(\omega)]$. The preionized electrons are then accelerated by the lower-frequency field $E(\omega)$ to obtain the maximum attainable kinetic energy $8U_p$. Thus for the phase $\phi=3\pi/2$ in the $\omega+3\omega$ excitation scheme, the net field is positive and large when the $E(\omega)$ field is minimum. This ensures large ionization of the electrons when the $E(\omega)$ field is weak, but it is to be noted that the sum of the fields adds constructively at the zeros of $E(\omega)$.

We show this effect by numerical integration of the time-dependent Schrödinger equation (TDSE) for one-dimensional (1D) H_2^+ and H_3^{2+}, following a numerical method previously described in [23]. This allows us to obtain, with high accuracy, ionization rates and HG spectra as a function of internuclear distance R, as shown in Figs. 1–4. The calculations are performed for the wavelength $\lambda=1064$ nm and intensity $I=10^{14}$ W/cm^2 for H_2^+ (Fig. 3) and for H_3^{2+} (Fig. 4). Results are presented for a 1D model (with regularized Coulomb potentials, $-[1+(x\pm R/2)]^{-1/2}$ [12,13]). The initial state for H_2^+ and H_3^{2+} is the completely *delocalized* ground $1\sigma_g$ orbital. Figure 1 shows large enhanced ionization of H_2^+ at the distance $R_c=8$. This peak corresponds to charge-resonance-enhanced ionization [10–12]. A minimum occurs also at $R=\pi\alpha_0/2=46$ a.u., where $\alpha_0=E/\omega^2=29$ a.u., the ponderomotive radius of the electron in the electromagnetic field. The H atom ionization rate, 1.3×10^{11} s^{-1}, is much less than the molecular ion at R_c, as emphasized above, but becomes the molecular rate at $R\simeq\pi\alpha_0$.

In Fig. 2 we illustrate the corresponding single-field excitation HG spectra for H and H_2^+ obtained by calculating the power spectrum from the laser-induced acceleration [10]. The maximum HG law (1) gives $N_{\max}\simeq 45$, as seen in Fig. 2(a) for the H atom. Figure 2(b) shows the HG spectrum for H_2^+ at $R=\pi\alpha_0/2=46$ a.u. A maximum is visible beyond the $3U_p$ law: $6U_p$ with $N\simeq 70$. Figure 2(c) shows the HG spectrum for $R=\pi\alpha_0=91$ a.u. There is a maximum around $8U_p$ ($N\simeq 90$) and a new cutoff arund $N\simeq 107$ for $10U_p$ energy,

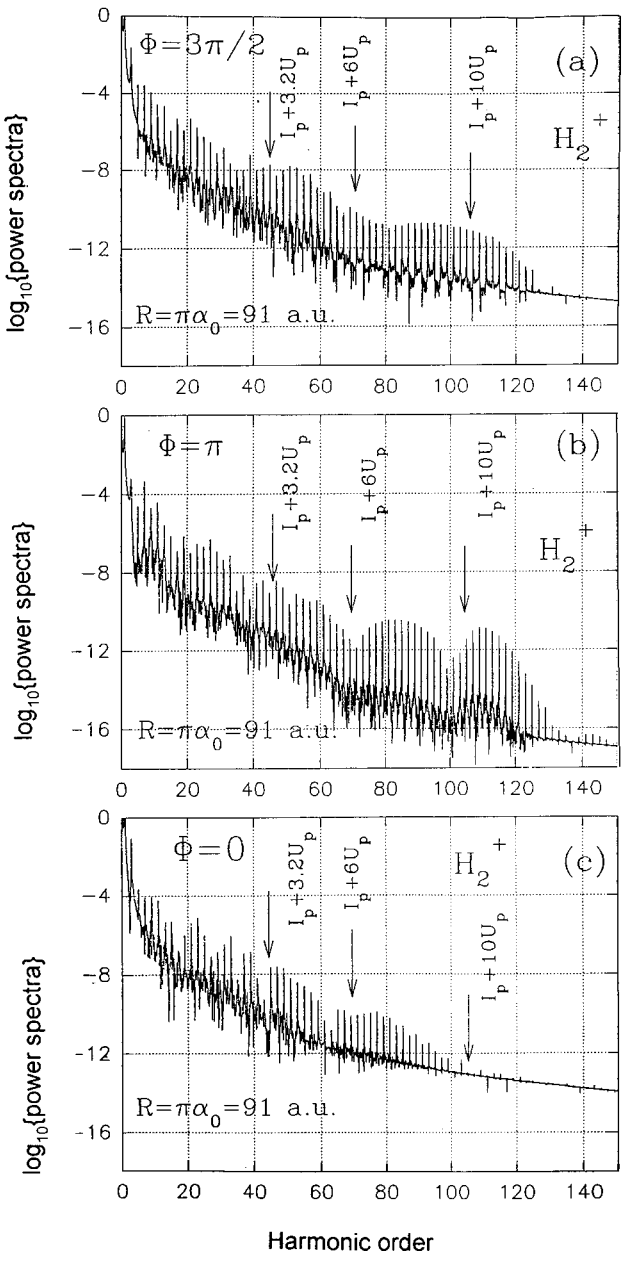

FIG. 3. H_2^+ harmonic spectra at $I=10^{14}$ W/cm^2, $\lambda=1064$ nm at $R=91=\pi\alpha_0$ a.u. for $E(t)$ [Eq. (4)]. (a) $\phi=3\pi/2$; (b) $\phi=\pi$; (c) $\phi=0$.

consistent with theoretical ATI spectra [18]. The $6U_p$ maximum at around $N\simeq 70$ still dominates the higher-order maxima and is always a new cutoff at $R=\pi\alpha_0/2$. Similar effects have been obtained in numerical simulations of the two-electron extended system H_2 and H_3^+ [24]. Using Eq. (1), one obtains for $Z=R=\pi\alpha_0/2$ that $\dot{Z}(t)=\pm 2U_p^{1/2}[1+\sin(\sin\omega t)]$ with the condition $\sin\omega t=\omega t-\pi/2$. The solution of the latter relation is $\omega t\simeq 3\pi/4$. The corresponding kinetic energy is $\dot{Z}^2/2=6U_p$, in agreement with Fig. 2(b). Thus Fig. 2 illustrates the increased energy available to electrons scattered by atoms separated at large distances relative to the single-atom case. The greater intensity of the $6U_p$ spectra with respect to $8U_p$ in Fig. 2(b) results from the fact that $8U_p$ kinetic energy is acquired for $\omega t=\pi$, with initial $\dot{Z}(0)=0$ at $|\phi|=\pi/2$. This implies that $8U_p$ electrons are

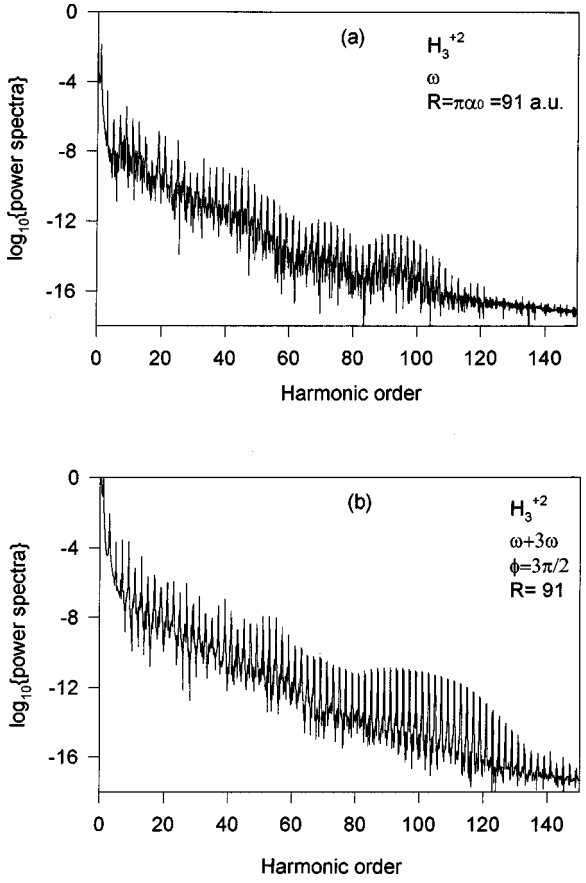

FIG. 4. H_3^{2+} harmonic spectra at $I=10^{14}$ W/cm^2, $\lambda=1064$ nm at $R=\pi\alpha_0=91$ a.u. (a) single field; (b) $\omega+3\omega$ [Eq. (4)], $\phi=3\pi/2$.

created when the field is nearly zero. $6U_p$ energy requires only that $\omega t=3\pi/4$, so that these electrons can be created when the field is nonzero, with resulting increased HG efficiency due to a high number of such electrons.

In order to increase HG efficiencies beyond $6U_p$, we use the combined ω and 3ω fields with variable phase ϕ ensuring increased ionization when the $E(\omega)$ field is weakest. The resulting HG spectra are illustrated in Fig. 3 at $R=\pi\alpha_0=91$ a.u. The $3U_p$ and $6U_p$ intensities are now enhanced over that of the single-field $E(\omega)$ excitation, Fig. 2, since ionization rates have been increased by at least one order of magnitude. The $8U_p$ region ($N\simeq 90$) is also clearly enhanced when compared to Fig. 2(c), the single laser excitation. A new region, $10U_p$ ($N\simeq 110$) with the two-color excitation scheme, also becomes prominent for $\phi=3\pi/2$ (ionization rate $\Gamma_i=9\times10^{12}$ s^{-1}), $\phi=\pi(\Gamma_i=3\times10^{12}$ s^{-1}) and $\phi=0(\Gamma_i=7\times10^{12}$ s^{-1}). The $\phi=0$ case, Fig. 3(b), has a large ionization rate due to the coincidence of $E(\omega)$ and $E(3\omega)$ peaks, but nevertheless produces less harmonics. In this particular case, there is no preionization at the zeros of $E(\omega)$. The net field $[E(\omega)+E(3\omega)]$ is very narrow around the peak value $1.5E_0$. Only $6U_p$ electrons seem to be enhanced in this case. We show next in Fig. 4 results for the one-electron extended system H_3^{2+} at the distance between outer protons 1 and 3, $R=91=\pi\alpha_0$ a.u. At short $R=6$ (equilibrium distance), the $3U_p$ law gives $N_{\max}\simeq 45$, similar to Fig. 2(a), whereas at $R=\pi\alpha_0$, single-laser excitation gives further maxima, Fig. 4(a). As seen from Fig. 4(b), the

$\omega+3\omega$ two-color excitation at $\phi=3\pi/2$ doubles the maximum number of harmonics with efficiencies only 10^{-2} lower than the $3U_p$ harmonics. The $\omega+2\omega$ schemes give very similar results, i.e., there is general overall enhancement of harmonic spectra intensities at $3U_p$, with the appearance of $6U_p$ and $8U_p$ photons comparable in intensity to the $3U_p$ photons at single excitation [24]. In both two-color excitations of H_2^+ and H_3^{2+}, high-order HG spectra are doubled in length and overall efficiency is increased by one or two orders of magnitude with respect to single-frequency excitation. We have found that the $\omega+3\omega$ two-color scheme gives the best efficiencies.

In conclusion, our numerical results based on the TDSE show that electrons accelerated by a short intense pulse should produce higher and more intense harmonics in polyatomic media such as molecules and clusters. Using a high-frequency prepulse ensures sufficient ionized electrons, which are then accelerated by a lower-frequency pulse in order to extend high harmonics beyond $3U_p$ up to $8U_p$ and $10U_p$ (see Figs. 3 and 4). Such a two-pulse technique should be particularly useful for the creation of high-order harmonics in rare-gas clusters [25], where the interatomic distances are already $R\sim 6-7$ a.u., the critical distance for CREI discussed above [10–13], and distant neighbors can be found abundantly at distances $R=\pi\alpha_0/2$ and $\pi\alpha_0$, which are reached by electrons with kinetic energies $6U_p$ to $10U_p$. For molecules, such an effect should be observable by first dissociating the molecule, letting the nuclei propagate to $R=\pi\alpha_0/2$ or $\pi\alpha_0$, and then ionizing with a second intense pulse [26].

We thank the Natural Sciences and Engineering Research Council of Canada for support of the present work and Dr. P. B. Corkum (NRC–Ottawa) and Dr. K. Lagatutta (Los Alamos) for useful discussions.

[1] J. J. Macklin, J. D. Kmetec, and C. L. Gordon, Phys. Rev. Lett. **70**, 766 (1993).
[2] A. L'Huillier and P. Balcou, Phys. Rev. Lett. **70**, 774 (1993).
[3] P. B. Corkum, Phys. Rev. Lett. **73**, 1995 (1993).
[4] J. L. Krause, K. J. Schafer, and K. C. Kulander, Phys. Rev. Lett. **68**, 3535 (1992).
[5] A. L'Huillier, M. Lewenstein, P. Salieres, P. Balcou, M. Y. Ivanov, J. Larsson, and C. G. Wahlström, Phys. Rev. A **48**, 3433 (1993).
[6] M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum, Phys. Rev. A **49**, 2117 (1994).
[7] R. Haight and D. R. Peale, Phys. Rev. Lett. **70**, 3979 (1993).
[8] J. Larsson, E. Mevel, R. Zerne, A. L'Huillier, C. G. Wahlström, and S. Svanberg, J. Phys. B **28**, L53 (1995).
[9] P. H. Bucksbaum (private communication).
[10] T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A **48**, 3837 (1993).
[11] T. Zuo and A. D. Bandrauk, Phys. Rev. A **52**, R2511 (1995).
[12] S. Chelkowski and A. D. Bandrauk, J. Phys. B **28**, L723 (1995).
[13] H. Yu and A. D. Bandrauk, Phys. Rev. A **56**, 685 (1997).
[14] T. Seideman, M. Y. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).
[15] Y. Liang, S. Augst, Y. Beaudoin, M. Chaker, H. Yu, A. D. Bandrauk, and S. L. Chin, J. Phys. B **28**, 3661 (1995).
[16] C. Lynga, A. L'Huillier, and C. G. Wahlström, J. Phys. B **29**, 3293 (1996).
[17] G. Paulus, W. Becker, and H. Walther, Phys. Rev. A **52**, 4043 (1995).
[18] G. Paulus, W. Nicklish, H. Xu, P. Lambropoulos, and H. Walther, Phys. Rev. Lett. **72**, 285 (1994).
[19] P. Moreno, L. Plaja, and L. Roso, J. Opt. Soc. Am. B **13**, 430 (1996); Phys. Rev. A **55**, 1593 (1997).
[20] T. Zuo and A. D. Bandrauk, Phys. Rev. A **54**, 3254 (1996).
[21] D. W. Schumacher, F. Weihe, H. G. Muller, and P. H. Bucksbaum, Phys. Rev. Lett. **73**, 1344 (1994).
[22] S. Watanabe, K. Kondo, Y. Nabekawa, A. Sagisaka, and Y. Kobayashi, Phys. Rev. Lett. **73**, 2692 (1994).
[23] S. Chelkowski and A. D. Bandrauk, Phys. Rev. A **46**, R5342 (1992).
[24] H. Yu and A. D. Bandrauk (unpublished).
[25] T. Donnelly, T. Ditmire, K. Neuman, M. D. Perry, and R. W. Falcone, Phys. Rev. Lett. **76**, 2473 (1996).
[26] H. Stapelfeldt, H. Sakai, E. Constant, and P. B. Corkum, Phys. Rev. A **55**, 3319 (1997).