Ultrahigh harmonic generation from diatomic molecular ions in highly excited vibrational states

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Numerical calculations of the harmonic yield from diatomic molecular ions initially prepared in a highly excited vibrational state show a remarkable enhancement of the harmonic energies in the *plateau* in terms of the ponderomotive energy. The two-step scheme that explains the mechanism of harmonic generation by atoms is extended to our double potential-well structure, providing an explanation for the high photon energies produced. [S1050-2947(97)50503-8]

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Many efforts in the study of laser interactions with matter have been focused on the atomic nonlinear radiative response to intense, low-frequency fields. One of the aims was to achieve coherent radiation sources at high frequencies, and high-order harmonic generation by gas targets has proved to be a very promising mechanism to reach that goal [1].

So far, the physical origin of the high photon energies in harmonic spectra from atoms has been well understood through both semiclassical and quantum approaches. A simple way to understand the process is the so-called two-step model [2–4]. According to this model, first the atoms are ionized by tunneling through the effective potential barrier. Then, the free electrons move back and forth driven by the periodic field and, as they return to the vicinity of the atomic core, they decay to bound states, releasing the acquired kinetic energy in the form of radiation of frequencies in odd multiples of the fundamental frequency. This model predicts photon energies up to $I_p+3.2U_p$, where I_p is the ionization potential and U_p is the mean kinetic energy of a free electron in the laser field. This is, in fact, the harmonic cutoff energy obtained in experiments with rare gases [1]. Similar nonlinear behaviors have been found in other materials, such as metals [5,6], dielectric surfaces [6], or molecular clusters [7], and some theoretical models have been proposed to explain the origin of the nonlinearity that gives rise to these radiative features [8–10]. Nevertheless, these systems have not revealed any symptom about the possibility of a considerable improvement of the maximum photon energies obtained from atoms in the tunnel ionization regime.

We have addressed in a previous work [11] a mechanism to overcome this limit for the cutoff energies in the case of a partially ionized gas in a strong linearly polarized field. There, the atom-ion pairs share the ionized electronic population. The main drawback of this proposal was the predicted low efficiencies for harmonics with energies beyond the single-atom limit, which prevents their experimental detection. This same scheme has been used by Donnelly *et al.* [7] in order to explain unexpected extra harmonic orders in the spectra produced by molecular clusters.

In this paper we study the harmonic generation by a diatomic molecular ion under the influence of an intense laser field. We shall demonstrate that a molecule stretched well beyond its equilibrium distance [12] yields harmonic peaks of much higher energies in units of the ponderomotive energy than those produced by an isolated atom or the same molecule in the lowest vibrational level. As we will show, large internuclear separation allows the electron to be detached from one of the cores, fly towards the partner, and release the energy absorbed from the field as it is captured by the latter. In the final part we discuss the apparent divergence between our results and those obtained in a tridimensional simulation by Zuo *et al.* [13] as well as the possibilities of experimental detection of such high-energy photons.

Our results are obtained by solving numerically the one-dimensional time-dependent Schrödinger equation for an electron moving in a potential consisting of two soft-core wells [11,14] and a periodic laser field $\mathcal{A}(t)$. We assume the Born-Oppenheimer approximation, which means neglecting the nuclear motion since the pulse duration is shorter than typical time scales for dissociation processes,

$$i\frac{\partial\psi}{\partial t}=-\frac{1}{2}\frac{\partial^2\psi}{\partial z^2}-i\frac{\mathcal{A}(t)}{c}\frac{\partial\psi}{\partial z}-\frac{Z}{\sqrt{a^2+\left(z-\frac{R}{2}\right)^2}}\psi$$

$$-\frac{Z}{\sqrt{a^2+\left(z+\frac{R}{2}\right)^2}}\psi. \qquad (1)$$

The depth, width, and separation of the cores are chosen to mimic diatomic molecular ions of the type $A_2{}^{n+}$ [15]. We assume that the field is linearly polarized and that the wells are aligned along the direction of polarization. Restricting the dynamics to one dimension means an artificial enhancement of all effects concerning both rescattering and recombination of electrons. This will exclude direct comparisons of our conversion efficiencies with experimental or tridimensional calculations, but if the field is intense enough the major features of the phenomenon must be preserved since it has been shown that the internuclear axis tends to be aligned with the direction of polarization [16].

The parameters of the molecular potential have been chosen in order to simulate the ion $H_2{}^+$ ($a=0.706$ Å, $Z=1$), so that the ground-state energy of the atom H agrees with that of the ion as the internuclear distance grows asymptotically

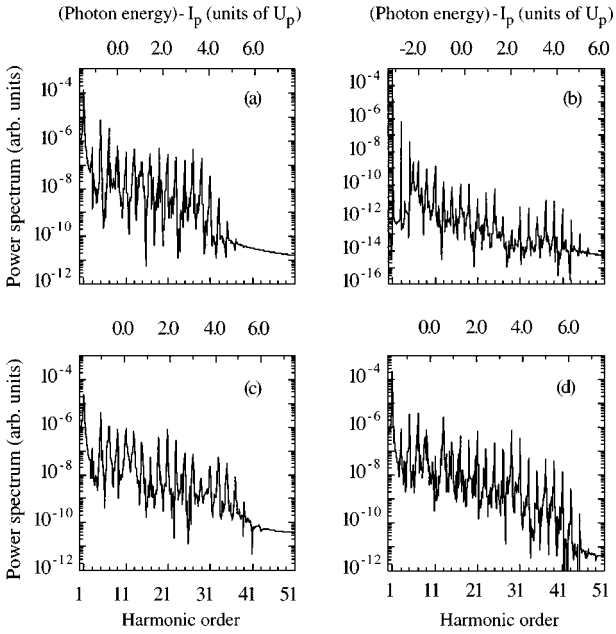

FIG. 1. Numerical calculations of harmonic spectra from one-dimensional H (a) and the molecular ion H_2^+ for internuclear distances, (b) $R=1$ Å, (c) $R=6$ Å, and (d) $R=10$ Å. The field was linearly ramped on three cycles followed by eight cycles of constant intensity $I=1.26\times10^{14}$ W/cm^2 and frequency $\omega=1.5$ eV ($\lambda=783$ nm). The upper axis, the difference between the photon energy and the ionization potential, shows that increasing R gives rise to a considerable enhancement of the photon energies in units of the ponderomotive energy.

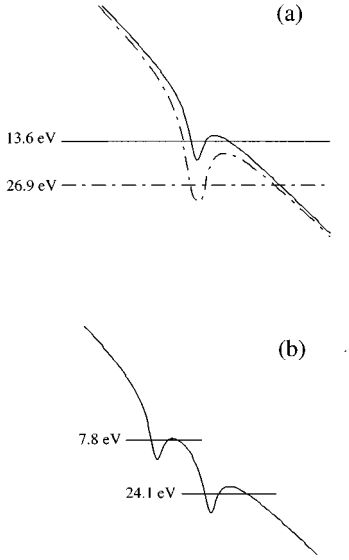

FIG. 2. A scheme of the effective potential ''seen'' by an electron for the maximum field amplitude as the field-free potential represents (a) the atom H (solid line) and the molecular ion H_2^+ in a low vibrational state ($R=1$ Å, dotted line); (b) H_2^+ in a high vibrational state ($R=6$ Å). The horizontal lines correspond to the dc-Stark shifted ground state energies. Obviously, internal ionization is likely only in the case (b) while in (a) ionization and, therefore, harmonic generation have to be atomiclike.

($R\rightarrow\infty$). In Fig. 1 we present a series of harmonic spectra corresponding to the atom H (a), the molecular ion H_2^+ whose internuclear distance is close to the equilibrium distance [(b) $R=1$ Å], and finally the same ion outstretched [(c) $R=6$ Å and (d) $R=10$ Å]. The laser pulse has a linear ramp turn-on of three cycles and then eight cycles of constant amplitude. The peak intensity of the field was set to 1.26×10^{14} W/cm^2 and the fundamental photon energy was $\omega=1.5$ eV ($\lambda=783$ nm) for all the cases. The pulse duration was 30 fs.

The most relevant feature of these spectra is the enhancement of the harmonic cutoff frequency for the stretched molecular ion [Figs. 1(c) and 1(d)] in comparison with both the atom [Fig. 1(a)] and the nonstretched molecular ion spectra [Fig. 1(b)]. The cutoff frequency ranges from the well-known value $I_p+3.2U_p$ for the atom to approximately $I_p+5.5U_p$ for the most outstretched ion. Since the field parameters, and so U_p, have not changed, it is rather obvious that the change in the system's structure as a result of the larger internuclear distance R is responsible for such an increase in the photon energies. In Fig. 2, a scheme of the effective potential acting on the electron as the field has reached its peak intensity for different values of R allows us to identify this change with the presence of a higher and higher potential barrier in between the nuclei. The width and height of this inner barrier depend on the separation between the nuclei and, in addition, increasing R means that the electron is less tightly bound, i.e., I_p is smaller. Therefore, it is important to realize that in contrast to a recent proposal by Watson *et al.* [17], the enlargement of the harmonic plateau in Fig. 1 happens despite the loss of harmonic orders resulting from the diminution of the binding energy of the electronic ground state with R. The absence of a spectacular increase in the number of harmonic orders throughout the plots in Fig. 1 in contrast to the corresponding increase of the cutoff frequency in units of U_p is another consequence of the diminution of the ionization potential.

The presence of a narrow internal barrier enables the flow of electronic population from one potential well to the other by a tunnel effect occurring at each half cycle of the electric field, although it has been recently reported [15,18,19] that under the influence of strong fields this transfer is mostly interrupted. In such conditions, part of the electronic population remains localized in the rising potential well and is freed through the inner barrier for enough intense fields. In Fig. 2(b) we show that this is the case for large values of R, while in the other two plots [Fig. 2(a)] this ionization mechanism is eventually not possible. Thus, in these latter cases harmonic generation should be understood as atomiclike since ionization does not differ from ionization in atomic systems. Actually, the magnitude of the ionization potential allows the electronic population to tunnel through the effective barrier in the case of the H atom ($I_p=13.6$ eV and the Keldysh parameter, $\Gamma=\sqrt{I_p/2U_p}=0.9$) while preventing a large tunnel ionization probability for the nonstretched H_2^+ ion ($I_p=26.9$ eV and $\Gamma=1.3$), as we show in Fig. 2(a). The harmonic energies extend to roughly $I_p+3.2U_p$ for both cases [Figs. 1(a) and (b)], although the harmonic efficiencies are very low for the nonstretched ion as a result of the low ionization probability. This confirms that in such a case, the ion generates harmonics like an atom.

On the other hand, as ionization through the internal barrier becomes a feasible mechanism—inasmuch as bound states have been strongly dc-Stark shifted permitting the detachment from the rising well of the effective potential [20–23] [Fig. 2(b)]—the electronic population ionized by means of this latter mechanism has a chance to reach the vicinity of the partner nucleus as a result of its motion driven by the electric field, and to radiate harmonics in the following process of scattering.

The mechanism for such harmonic production should be analogous to the generation by an isolated atom. On this basis, we will apply the two-step model to understand the ultrahigh photon energies in the spectra of Fig. 1. In this model, the harmonic cutoff frequency in atomic spectra is determined by the maximum kinetic energy that a detached electron has when it returns to the vicinity of the atomic core driven by the electric field, i.e., $3.2U_p$. The magnitude of this energy has been calculated assuming that tunnel ionized electrons behave as classical particles driven by the intense field and neglecting the influence of atomic potential on ionized electrons [3]. This simple model is also successful in explaining the high energies of electrons in experimental and numerical ATI spectra from atoms [24,25] invoking backscattering processes for tunnel ionized electrons. The classical formula for the instantaneous kinetic energy of rescattered electrons is

$$E_{\mathrm{kin}}=2U_p[2\cos\omega t_{\mathrm{res}}-\cos\omega t_{\mathrm{ion}}-\cos\omega t]^2, \qquad (2)$$

where t_{ion} is the instant of ionization and t_{res} the instant of the first backscattering. The photoelectron energies in the ATI spectra range up to $10U_p$ because of backscattering. Even if tunnel ionized electrons do not undergo rescattering processes, their kinetic energies oscillate together with the electric field from 0 to a maximum value, which depends on the instant of ionization as is obvious from the corresponding classical equation [Eq. (3)],

$$E_{\mathrm{kin}}=2U_p[\cos\omega t-\cos\omega t_{\mathrm{ion}}]^2. \qquad (3)$$

Given the instant of ionization, the electron will acquire its maximum kinetic energy periodically in time and space if it is only driven by the electric field. Figure 3 displays these maximum kinetic energies as a function of the distance (circles) to the position of the atomic core in units of the classical excursion of the electron in the field $\alpha_0=E_0/\omega^2$ and assuming any value of t_{ion}. Energies up to $8U_p$ are available at distances given by $m\pi\alpha_0$, where m is an odd integer [11]. These electrons contribute to the most likely energies in the atomic ATI spectra, i.e., up to $2U_p$. Therefore, we shall consider the effect of electrons flying directly to the partner rather than those that could undergo previous backscattering processes.

Coming back to H_2^+ and assuming that the electron detached through the inner barrier is barely affected by the molecular potential along its trajectory in between the nuclei, we can extend the two-step scheme in order to quantify the harmonic frequencies produced while this electron scatters with the partner. In Fig. 3 we compare the harmonic cutoff frequencies in the spectra of one-dimensional H_2^+ for a wider range of internuclear distances than in Fig. 1, with the classical expected maximum kinetic energies for electrons

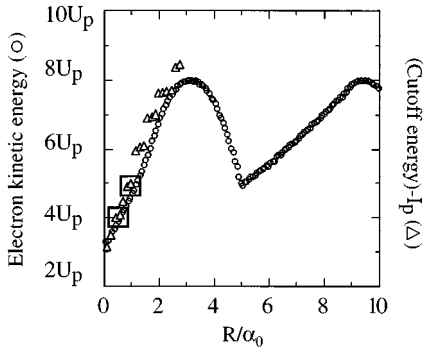

FIG. 3. Comparison of the expected classical maximum kinetic energies for the tunnel ionized electron encountering the partner nucleus at different distances (circles) and the harmonic cutoff energies calculated by numerical solution of the Schrödinger equation for one-dimensional H_2^+ with different fixed internuclear distances (triangles). We take α_0 as a unit of internuclear distance. The squares mark the region corresponding to the internuclear distance R of Figs. 1(c) and 1(d). The field is the same as Fig. 1 and $\alpha_0\approx 10$ Å.

ionized through the inner barrier and flying directly to the partner nucleus. Each triangle corresponds to an exact numerical calculation of the harmonic cutoff for a fixed value of R. The agreement between the curves confirms our hypothesis and provides an estimation of the expected cutoff frequency for a given pulse and internuclear distance. We have remarked upon the regions corresponding to the cases (c) and (d) of Fig. 1, for which the ratio R/α_0 has the value 0.6 and 1, respectively. Of course, the expected harmonic cutoff in these figures is still far from the maximum value $8U_p$ since the precedent ratio is far from $\pi\alpha_0$ as well.

Therefore, detecting harmonics beyond the single-atom cutoff frequency requires an appreciable ratio between the internuclear distance R and the classical excursion of the electron in the field α_0. Of course, if R is very small compared with α_0, the ionized packet cannot acquire energies so high and the cutoff should remain close to $I_p+3.2U_p$. This is the explanation for the absence of higher harmonic peaks in tridimensional calculations performed in Ref. [13]. They assumed very small R in comparison with α_0, and therefore the harmonic energies differed slightly from those predicted by the single-atom law.

In conclusion, molecular ions in high excited vibrational states provide a source to generate much higher frequencies than atoms in terms of U_p. These high-order harmonics should be observable in tridimensional simulations and experiments whenever the joint effect of a large internuclear distance and an intense field allows the electronic population to fly from the parent nucleus to the partner through the continuum states. In fact, since the main role in this ultrahigh harmonic generation is played by the multiple-well structure of the molecular potential, it should be observable in any molecule under the conditions pointed out before. The experimental results by Donnelly *et al.* [7] working with molecular clusters are encouraging. They present an increment of the number of harmonics in Ar clusters as well as an enhancement of the harmonic efficiency as compared to the monomer case. The distance between Ar neighbors is 3.7 Å, while the intensities assure they are in the tunnel ionization

regime. Whether these increments of the number of harmonics are related to the presence of close partners could be tested by looking at high-order harmonics when an intense laser field irradiates a low-density molecular cluster.

The study of the harmonic spectra of diatomic molecular ions with the nuclei located at intermediate distances promises to offer interesting new features. This is the range of distances where Chelkowski *et al.* [26] and recently Seidemann *et al.* [15] found that the molecular ionization rate exhibits a considerable enhancement. It is reasonable to think that this should affect the harmonic efficiencies but also the expected photon energies since the internal barrier is suppressed for the electronic population.

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