Multichannel Molecular High-Order Harmonic Generation from Asymmetric Diatomic Molecules

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Multichannel molecular high-order harmonic generation (MHOHG) from a single electron asymmetric molecular ion HeH^{2+} is investigated numerically. It is found that considerable resonant excitation occurs by laser induced electron transfer (LIET) to neighboring ions and multiple frequency (fractional-order) harmonics are observed from the excited states shifted by some energy Δ from the main $N\omega$ energy harmonics. A time series analysis is used to confirm this MHOHG channel which is created by initial ionization from the excited state prepared by LIET and recombination to the neighboring ion at specific field phases, resulting in interference between recombination pathways from ground and excited states.

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The interaction between intense ultrashort few cycle laser pulses and atoms [1,2] and molecules [3] has received considerable attention recently. Many novel nonlinear nonperturbative phenomena have been discovered, such as, for example, high-order harmonic generation (HHG), which has become an important tool to generate coherent attosecond laser pulses [4]. Currently, a semiclassical three-step model is used to interpret the HHG mechanism for initial zero velocity ionized electrons [5] and nonzero velocity electron [6]. The electron can be ionized by tunneling from the ground state, then is accelerated by the laser field, and returns back to the original ion to recombine with the parent ion and emit HHG photons. This model is successful to explain the maximum cutoff energy $I_p + 3.17U_p$ of HHG observed in atoms and molecules [3], where the lifetime of excited states are comparably short in intense laser fields. However, for asymmetric charged molecules, such as HeH^{2+} and LiH^{3+}, which have permanent dipoles and multiple centers, the excited states maybe localized states and their lifetime may be comparably long. For example, the electronic probability wave function of the $1s\sigma$ ground state of HeH^{2+} is mainly localized on the He^{2+} ion, while the electronic probability of the first excited state $2p\sigma$ is mainly on the H^+. The ground state is repulsive, while the first excited state is a bound state with a minimum at $R = 3.89$ a.u. [7]. The mean lifetime of the first excited $2p\sigma$ state of HeH^{2+} is about 4 ns [7]. In this case, there can be comparable population created on ground and low excited states in intense laser pulses. HHG from coherent superposition of atomic states has been considered previously [8]. We show here one must take the role of excited states into account for molecular high-order harmonic generation (MHOHG) in asymmetric molecular ions in intense laser fields. In fact, it has been reported recently that bright harmonics can be emitted from multiply charged ions due to their larger I_p [9]. In this Letter, we use the simplest asymmetric molecular ion HeH^{2+} to investigate the role of excited states in MHOHG. Previous work on atoms has shown that excited states can enhance harmonic yields [10,11]. We show novel effects appear in nonsymmetric molecules due to laser induced electron transfer (LIET) [12].

We have calculated the MHOHG spectrum of HeH^{2+} by numerically solving the corresponding time-dependent Schrödinger equation (TDSE) (in atomic units, $e = m = \hbar = 1$): $i\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = [H_0 + H(t)]\Psi(\mathbf{r}, t)$ in the Born-Oppenheimer approximation, using our previously developed B-spline symplectic method [13] in prolate spheroidal coordinates. The MHOHG spectrum is obtained by the Fourier transform of the dipole momentum in the acceleration form $d_A(t) = -\langle\Psi(t)|\partial V/\partial z + E(t)|\Psi(t)\rangle$.

(i) Enhanced excitation.—For the asymmetric molecule HeH^{2+}, odd and even order harmonics will appear due to broken symmetry. We have calculated the MHOHG spectra of HeH^{2+} with pulses of time duration 10 optical-cycle trapezoidal shape with 3 cycles ramp on, 4 cycles constant, and 3 cycles ramp off. The results are shown in Fig. 1 at two wavelengths: 532 and 400 nm. For these different laser wavelengths and intensities, the Keldysh parameter $\gamma \approx 1$, corresponding to the tunneling ionization regime [1]. At the internuclear distance $R = 4$ a.u., the field-free energy of the ground state of HeH^{2+}: $E_{1s\sigma} = -2.2506$ a.u. $\approx -I_p(He^+) - 1/R$. The MHOHG spectrum at wavelength 532 nm with intensity $I = 1.5 \times 10^{15}$ W/cm^2, is presented in Fig. 1(a). From the spectrum, we can clearly see a strong resonance around harmonic order 20. To identify this strong resonance, we use the exterior complex scaling (ECS) B spline method [13] to calculate the dressed energies of the ground and first excited state in a dc field, $H = H_0 + Fz$. The electric field amplitude $|F|$ corresponds to the peak laser intensity. By rotating the coordinate $\xi \rightarrow (\xi - \xi_0)e^{i\theta}$ in the outer region ξ_0, where θ is the rotation angle, after a diagonalization, we obtain the dressed complex energy $E = E_R - i\Gamma/2$. The real part E_R corresponds to the Stark shifted energy, while the imaginary part Γ is the resonant width connected to the ionization rate [14]. We show the dressed ground and first excited state energy in Figs. 2(a) and 2(b) with their com-

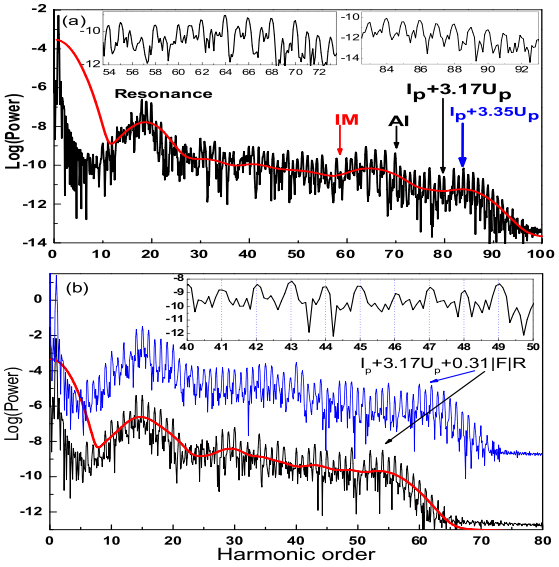

FIG. 1 (color online). MHOHG spectra of HeH^{2+} in intense laser field. The internuclear distance is fixed at $R = 4$ a.u. The solid line (red) is a smoothed spectrum. In (a), the laser field is with wavelength 532 nm and peak intensity 1.5×10^{15} W/cm^2. The inset is the enlarged area in plateau and cutoff region. In (b), the laser field is with wavelength 400 nm and peak intensity 2×10^{15} W/cm^2 (lower black line), and intensity 2.5×10^{15} W/cm^2 (upper blue line), respectively. For comparison, the harmonics at 2.5×10^{15} W/cm^2 is shifted up by 2.5 orders. The inset is the enlarged area of the harmonic spectrum from order 40 to 50 at 2×10^{15} W/cm^2.

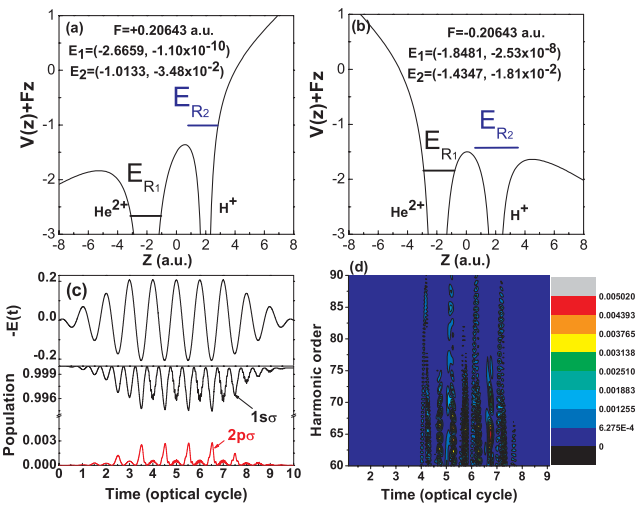

FIG. 2 (color online). (a) and (b) is combined Coulomb and static field potential for $F > 0$ and $F < 0$, respectively, with dressed energies. The static field strength F corresponds to the peak laser intensity of Fig. 1(a). (c) is the laser field and population of $1s\sigma$ and $2p\sigma$ state as a function of laser cycle. (d) is the time profile of MHOHG spectrum in Fig. 1(a) from order 60 to 90.

plex energies. For this asymmetric molecule, the ionization rate and the dressed energy are quite different for a dc field along the $+z$ or $-z$ molecular axis. For $F > 0$, the ground state energy $E_{R_1} = -2.6659$ a.u. is Stark shifted *downward*, the energy gap $\Delta = E_{R_2} - E_{R_1} \approx 19.3\omega$ is large, and the ionization rate $\Gamma_1/2 = 1.1 \times 10^{-10}$ a.u. is about two orders lower than the case $F < 0 (\Gamma_1/2 = 2.53 \times 10^{-8}$ a.u.). For $F < 0$, the ground state energy $E_{R_1} = -1.8481$ a.u. is Stark shifted *upward*, and the energy gap $\Delta = E_{R_2} - E_{R_1} \approx 4.8\omega$ is small. In this case, the ionization rate is high, and it has more chance to pump the system from ground state to excited states by near resonant tunneling [Fig. 2(b)]. This effect has been reported previously by Kamta and Bandrauk and is responsible for enhanced ionization (EI) [15]. We show next in this nonsymmetric system the population of the $1s\sigma$ and $2p\sigma$ states of HeH^{2+} in a 532 nm laser field in Fig. 2(c). The enhanced excitation is obvious for $F < 0$. When the laser field changes its direction, the electron will transit back to the ground state. The resonance position in the MHOHG at around 20ω at 532 nm agrees well with the calculated energy gap $\Delta = E_{R_2} - E_{R_1} \approx 19.3\omega$ between the shifted first excited state E_{R_2} and the ground state energy E_{R_1} at $F > 0$ [shown in Fig. 2(a)]. The intensity of this resonance is about 4 order higher than the harmonics in the plateau. Similar resonance around 15ω at 400 nm is also clearly observed in Fig. 1(b).

It is a general feature of enhanced excited system. Similar resonance is observed in plasma ablation [16], but the resonance position seems not sensitive to the laser intensity. For HeH^{2+}, the position of the strong resonance is dependent on the shifted energy gap, which is determined by the laser intensity. In conclusion, one can change the laser intensity to control the position of the bright high-efficiency harmonic generation around the strong resonance.

ii) Double plateau by LIET.—A new feature appears in Fig. 1(a), where we observe two clear plateaus before and after harmonic order 70. The latter is about one order weaker in intensity than the lower harmonics. We use a Gabor analysis [17,18] of the spectra: $d_G(\omega, t) = \int_0^T \exp(-i\omega t') \exp[-\frac{(t'-t)^2}{2\sigma_0^2}] d_A(t') dt'$, where $d_A(t)$ is the time-dependent dipole momentum in acceleration form, σ_0 is the width of the Gaussian time window to analyze electron transitions in the spectrum. The time profile of harmonic order from 60 to 100 is illustrated in Fig. 2(d). From the figure, it is obvious that the time profile of collision is weaker at field $F < 0$ in the second plateau. The reason is that the collision electron at field $F < 0$ is created one-half of a cycle earlier at $F > 0$ by ionization. As mentioned above, the ionization rate at field $F > 0$ is about 2 orders lower than $F < 0$. Consequently, the electron which is ionized at field $F > 0$, after about half a laser cycle later, in the corresponding recombination process of MHOHG which happens at field $F < 0$ emits less photons. This two-plateau structure in MHOHG in the 400 nm laser field also appears in Fig. 1(b), as a result of asymmetric ionization along the molecular axis. Since this asymmetry is inherent in nonsymmetric molecules, the double-plateau structure in MHOHG is clearly a general feature in asym-

metric systems due to LIET [12]. Such a double-plateau structure has been reported before in atomic coherent superposition state [8], but we emphasize that in nonsymmetric molecules this is due to LIET [12]. Another important feature from Fig. 1 is that the cutoff energy is larger than the classical $I_p + 3.17U_p$ law. We observe a clear small minimum at $I_p + 3.17U_p$. However, the cutoff region extends to $I_p + 3.35U_p$ in Fig. 1(a). From the three-step model, if the electron recombines with the parent ion core, the maximum energy of the electron obtained from the laser field is $3.17U_p$ [5,6]. One may argue that this new cutoff comes from the quantum effects [19]. However, for high frequency laser field and large bound potential system, we propose that the new extended cutoff at $I_p + 3.35U_p$ comes from the different field potential energies between the ionization ion and recombination ion [20,21]. To identify this channel, we use a 1D semiclassical recollision model [5,6]. The electron with kinetic energy $3.17U_p$ comes back to its origin with phase $\phi \approx 1.4\pi$. If the electron ionized from the first excited state at $z = +2$ a.u. corresponding to H^+, is accelerated in the laser field, and recombines with the ground state at $z = -2$ a.u. at He^{2+}, it will acquire larger kinetic energy owing to a longer acceleration time by the laser field as it crosses the whole molecule. There also is a small chance that the election ionized from $z = -2$ a.u.(He^{2+}), recollides at $z = +2$ a.u.(H^+), and then transits to the ground state. The extra kinetic energy is about $\Delta E_k \approx |E|R \approx |F\cos(1.4\pi)|R \approx 0.31|F|R \approx 0.176U_p$. This is due to the effect that the ionization origin and recombination site are separated by R and therefore have different potential energy $0.31|F|R$. Simulations at a laser field with different wavelength 400 nm and intensities [presented in Fig. 1(b)] gives an extension of the cutoff energy up to $I_p + 3.17U_p + 0.31|F|R$, which confirms our interpretation. To further investigate the recombination process, we have solved the 1D classical Newton equations numerically, and obtained the recollision energy and time for free electron in the laser field shown in Fig. 1(a). For the internuclear distance $R = 4$ a.u., the maximum energy obtained by this collision from the laser field is $3.35U_p$ by the classical simulations in Fig. 3(c) and agrees well with the quantum calculation. The recollision time of harmonic order $N = 84$ obtained by classical simulations is marked in Fig. 3(d) as arrows. A Gabor time analysis of harmonic order 84 in the cut-off region is also shown in Fig. 3(d). We can see the recollision time from the TDSE agrees well with the classical simulation.

iii) Multiple frequency harmonic series.—The channel for electron ionization from the excited state and recombination to the ground-state mechanism provides not only an extended cut-off but also new multiple frequency or fractional-order harmonic series. From the inset of Fig. 1(a), fractional-order harmonics are resolvable as occurring between peaks in a dominant harmonic series energy $N\omega$ corresponding to a new energy $\Delta + N\omega$ in the

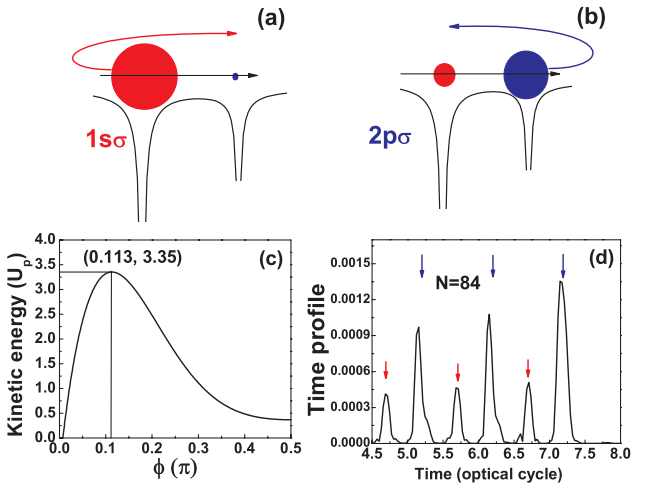

FIG. 3 (color online). (a) and (b) is schematic illustration of collision processes of $1s\sigma$ and $2p\sigma$ states from one well to the other well. (c) is the collision kinetic energy of electron obtained from the laser field as a function of the phase when it is ionized. (d) is the time profile of harmonics order 84 of Fig. 1(a). The arrows correspond to the collision time from 1D classical model.

plateau and cutoff region. Fractional-order harmonics are generated by a periodic laser field, which is counterintuitive. We have checked our numerical results using split-operator and Arnoldi-Lonczos methods [22] in both length and velocity gauges. The fractional-order harmonics remain confirming the accuracy of our method. To explain the mechanism of the fractional harmonic generation, we assume the electron is ionized by absorbing $N\omega$ photon energies from the first excited state when the laser field is at its maximum amplitude, while the field is approximately 0 when the electron returns back. For the laser field in Fig. 1(a), the dressed energy of the first excited state for $F < 0$ is shown in Fig. 2(b), $E_{R_2} = -1.4347$ a.u. When the electron returns back to the ground state, we take the energy of the ground state as the field-free energy $E_{1s\sigma} = -2.2506$ a.u., and the energy gap $\Delta = E_{R_2} - E_{1s\sigma} = 9.52\omega$. Therefore, $\Delta + N\omega$ corresponds to the energy of the new set of fractional harmonics. Generally, if the ionized electron absorbs $N\omega$ photon energies from the dress excited state at $F > 0$, there should be another set of fractional harmonics with energy $\Delta' + N\omega$, because the shifted energy E_2 is different. However, as discussed above, due to the large energy gap (19.3ω) at $F > 0$, the excitation rate is quite low, so this channel is not obvious for HeH^{2+} at 532 nm excitation. However, if we increase the photon energy, or increase the laser intensity, the channel at $F > 0$ may be identified. This occurs at 400 nm as shown in the inset of Fig. 1(b). We clearly identify these two channels from the excited state along $F > 0$ and $F < 0$ direction. The calculated $\Delta = 6.5\omega$ at $F < 0$ and $\Delta' = 10.6\omega$ at $F > 0$ correspond to two new sets of fractional harmonics with energy $\Delta + N\omega$ and $\Delta' + N\omega$, which agrees well with our prediction. To our knowledge, these fractional-order harmonics even in the cut-off

region of MHOHG is reported for the first time. Because of this frequency mixing, we suggest this effect can be used to generate complex attosecond laser pulses.

(iv) Interference.—Attosecond pulses may be used to map and study attosecond electron wave packet motion [23]. For the asymmetric molecule HeH^{2+}, the harmonics, generated by LIET from excited states (e.g.. from H^+) and recombined with the ground state (He^{2+}), will have a phase difference $\delta\phi$ with the harmonics obtained by ionization and recombination with the same parent atomic ion. This phase will lead to destructive interference when the internuclear distance $R = (2m + 1)\lambda_e/2$, $m = 0, 1, 2, \ldots$, where λ_e is the electron wavelength. In symmetric H_2^+ and H_2, one assumes $E_k = \hbar\omega$, because the potential energy will convert to kinetic energy when the electron recollides with the parent ions where the interference happens [15,24]. However, in the model HeH^{2+}, this interference comes from the phase difference between MHOHG channels from ground and excited states due to LIET. After the electron is ionized, it is approximately a free electron. For MHOHG from the ground state, the electron ionized from the ground state $1s\sigma$ leaves the He^{2+} ion and recombines with He^{2+}. For MHOHG from the first excited state, the electron ionized from the state $2p\sigma$ leaves H^+ and recombines with the He^{2+} as illustrated in Fig. 3(b). The continuum electrons have therefore two different pathways which will interfere with each other as continuum states. We use $E_k = \hbar\omega - I_p$ as the continuum energy in our analysis. The smoothed MHOHG spectrum is presented in Fig. 1(a) by a solid line. Taking the 532 nm laser field as an example, for $m = 0$, the first interference minimum (IM) should be around harmonic order 30, but this minimum is too close to the ionization threshold and the strong resonance to be clearly identified. For $m = 1$, the minimum of HHG is predicted to be around order 58. This prediction which assumes an electron phase $\Delta\phi$ is accumulated by recombination with He^{2+} after ionization from the $2p\sigma$ state, i.e., $H(1s)$, agrees well with our spectra. We can see a clear minimum in Fig. 1(b) around order 58. We also find that, for harmonics from 58 to 70, the *even* order harmonics are higher in intensity than *odd* order harmonics. For the atom argon, Dudovich *et al.* [25] observed the modulation of even order harmonics as a function of time delay between the fundamental and weak second-harmonic fields. For HeH^{2+}, the phase difference between harmonics from the ground state and excited state plays a similar role in the competition between even and odd order harmonics. For a 400 nm laser pulse, the minimum should be around order 22 and 43, which agrees well with our calculation in Fig. 1(b) for laser intensity 2×10^{15} W/cm^2. However, this interference between the channels from ground state and excited state is not robust. Only when the amplitude of the electron from these two channels are comparable, the interference will occur.

In summary, we have studied multichannel MHOHG from the asymmetric HeH^{2+} in few cycle intense laser pulses. An extended cutoff of harmonic spectra is observed numerically and confirmed by a classical collision and recombination dynamics with neighboring ions. This channel also leads to new energy harmonic generation series $\Delta + N\omega$, where Δ is the energy separation between the ground state and the excited state prepared by LIET. We propose thus a new way to generate complex attosecond pulses due to the generation of multiple series of harmonics shifted by the energy Δ. To our knowledge, this multiple frequency harmonic generation and the interference between pathways of MHOHG from the ground and excited state in asymmetric molecule due to LIET is predicted for the first time. The strong orientation effect for asymmetric ionization is also demonstrated in MHOHG spectra by a double-plateau structure, which should be an inherent feature for nonsymmetric system.

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