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High-order harmonic generation and multi-photon ionization of Na_2 in laser fields*

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In this paper high-order harmonic generation (HHG) spectra and the ionization probabilities of various charge states of small cluster Na_2 in the multiphoton regimes are calculated by using time-dependent local density approximation (TDLDA) for one-colour (1064 nm) and two-colour (1064 nm and 532 nm) ultrashort (25 fs) laser pulses. HHG spectra of Na_2 have not the large extent of plateaus due to pronounced collective effects of electron dynamics. In addition, the two-colour laser field can result in the breaking of the symmetry and generation of the even order harmonic such as the second order harmonic. The results of ionization probabilities show that a two-colour laser field can increase the ionization probability of higher charge state.

Keywords: high-order harmonic spectra, ionization probabilities, TDLDA
PACC: 3640C, 4250, 6120L

1. Introduction

High-order harmonic generation (HHG) is a coherent interaction process between atoms or molecules and a driving laser field, and produces ultrashort coherent radiation reaching the soft x-ray region. The application of a two-colour laser field for HHG has been a fascinating topic of research since recent developments in laser technology have made it possible to produce laser pulses with variable and controllable amplitudes and phases even in the ultrashort ($t < 10$ fs) and intense regime ($I \geq 10^{14}$ W/cm^2).[1,2] A simple superposition of a field of frequency ω and its second harmonic, with total field

$$E(t) = E_0(t)[\sin(\omega t) + f\sin(2\omega t + \phi)], \qquad (1)$$

where $E_0(t)$ is the field envelope, ϕ the relative phase, and f the relative amplitude. Equation (1) has been applied to atoms,[2−4] molecules[5−9] and clusters.[10] By changing the relative phase between the fundamental frequency and its second harmonic fields in the two-colour laser fields, one can control the output, such as the formation of harmonic spectrum and yields of ion or molecular fragments. Experimental and theoretical investigations on harmonic generation in the two-colour laser fields reported the generation of all integer-order harmonics due to the breaking of inversion symmetry, an especially large enhancement of harmonic signal and significant change of the ionization and dissociation probabilities due to the relative phase change. While HHG has been well studied for atoms, much less has been done for molecules. Extension of such simulations to multi-electron systems is of great interest, but can only be achieved by replacing the multidimensional time-dependent Schrödinger equation (TDSE) with effective single electron theories such as density functional theory (DFT)[11] and its extension to the time-dependent regime, time-dependent density functional theory (TDDFT).[12] The electron dynamics of Na clusters have been widely studied,[13−16] it is shown that time-dependent local density approximation (TDLDA) and TDLDA-self-interaction correction (SIC) give similar results for observables such as ionization rates and HHG spectra. But the effects of two-colour laser fields on Na cluster have been less studied.

In this paper, we use TDLDA methods to investigate the above-threshold ionization and harmonic generation of small cluster Na_2 in two-colour laser fields.

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2. Theory

According to the Kohn–Sham single electron orbit theory,[11] interacting multi-electron system can equivalently be described through the system of noninteracting electrons with the same density. In principle, the time-dependent density can be obtained through a set of non interacting single-electron wavefunctions $\phi_j(\boldsymbol{r},t)$ which satisfy the time-dependent Kohn–Sham (TDKS) equation,

$$\begin{aligned} \mathrm{i}\frac{\partial}{\partial t}\phi_j(\boldsymbol{r},t) &= \widehat{H}_{Ks}\phi_j(\boldsymbol{r},t) \\ &= \Big(-\frac{\nabla^2}{2} + V_{\mathrm{eff}}(\boldsymbol{r},t)\Big)\phi_j(\boldsymbol{r},t), \\ & j = 1,2,3...N. \end{aligned} \tag{2}$$

The TDKS effective potential V_{eff} is decomposed into an ionic background potential $V_{\mathrm{ion}} = \sum_I V_{\mathrm{ps}}(\boldsymbol{r} - \boldsymbol{R}_{\mathrm{I}})$ from the ionic core at positions $\{\boldsymbol{R}_{\mathrm{I}}\}$, external force potential V_{laser}, a time-dependent Hartree part V_{H} and a so-called exchange-correlation (xc) potential V_{xc},

$$\begin{aligned} V_{\mathrm{eff}}[n](\boldsymbol{r},t) &= V_{\mathrm{ion}}(\boldsymbol{r},t) + V_{\mathrm{laser}}(\boldsymbol{r},t) \\ &\quad + V_{\mathrm{H}}[n](\boldsymbol{r},t) + V_{\mathrm{xc}}[n](\boldsymbol{r},t), \end{aligned} \tag{3}$$

where the electronic density n is written by

$$n(\boldsymbol{r},t) = \sum_{j=1}^{N} |\phi_j(\boldsymbol{r},t)|^2, \tag{4}$$

and the Hartree potential $V_{\mathrm{H}}[n](\boldsymbol{r},t)$ is defined as

$$V_{\mathrm{H}}[n](\boldsymbol{r},t) = \int \mathrm{d}^3 r' \frac{n(\boldsymbol{r}',t)}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{5}$$

The xc potential $V_{\mathrm{xc}}[n](\boldsymbol{r},t)$ is a functional of the time-dependent density and has many approximation choices. In this paper, we use the simplest approximation TDLDA, which is defined as

$$V_{\mathrm{xc}}^{\mathrm{TDLDA}}[n](\boldsymbol{r},t) = \mathrm{d}\epsilon_{\mathrm{xc}}^{\mathrm{hom}}(n)/\mathrm{d}n|_{n=n(\boldsymbol{r},t)}, \tag{6}$$

where $\epsilon_{\mathrm{xc}}^{\mathrm{hom}}(n)$ is the xc energy density of homogeneous electron gas, for which the parametrization of Perdew and Zunger is used.[17] The norm-conserving pseudopotentials v_{ps} in the fully separable forms are constructed by the method of Troullier and Martins.[18]

The TDKS equations are integrated with simple second-order difference (SOD) scheme,

$$\phi_j(t + \Delta t) = -2\mathrm{i}\Delta t \widehat{H}_{\mathrm{KS}}(t)\phi_j(t) + \phi_j(t - \Delta t), \tag{7}$$

which is accurate to the second order of Δt. To evaluate the kinetic Laplacian operator, we use the technique of fast Fourier transform (FFT) which is quite efficient and accurate. The single-electron orbits $\phi_j(\boldsymbol{r},t)$ are no longer orthogonal to each other due to the existence of the calculation error, and must be re-orthogonalized. In the SOD scheme, the error in the propagation accumulates in the phase of wave function $\phi_j(\boldsymbol{r},t)$. This scheme has successfully used in Refs.[19, 20].

To calculate the HHG and multi-photon ionization of a cluster Na_2, we apply an external field, $V_{\mathrm{laser}}(\boldsymbol{r},t) = E(t)x$ ($E(t)$ is defined in Eq.(1) for a two colour laser which is polarized along x direction, the direction of the symmetry axis connecting two atoms of Na_2). Having obtained the electron density, we can calculate the changes of dipole moment in x, y, z directions

$$\delta D_i(t) = D_i(t=0) - \int \mathrm{d}^3 r r_i n(\boldsymbol{r},t), \quad i = x,y,z, \tag{8}$$

and the high-order harmonic spectrum which is related to the Fourier transform $S_i(\omega')$, with

$$S_i(\omega') = |2\int_0^\infty \delta D_i(t)\cos(\omega' t)\mathrm{d}t|^2, \quad i = x,y,z. \tag{9}$$

An average over the three excitations along x, y, and z directions is obtained

$$S(\omega') = (1/3)\sum_{i=x,y,z} S_i(\omega'). \tag{10}$$

The number of emitted electrons is defined as $N_{\mathrm{esc}}(t) = N(t=0) - \int_V \mathrm{d}^3 r n(\boldsymbol{r},t)$, where V is a volume surrounding cluster. Ionization probabilities $P^k(t)$ of the clusters at a time t in one of the possible charge states k can be obtained by making use of Ullrich formula.[21] In Na_2 case, the possible charge states are $P^0(t) = N_1(t)N_2(t)$, $P^+(t) = N_1(t)(1 - N_2(t)) + N_2(t)(1 - N_1(t))$, $P^{2+}(t) = (1 - N_1(t))(1 - N_2(t))$, where bound state occupation probabilities $N_j(t)$ are associated with the single particle Kohn–Sham densities $n_j(\boldsymbol{r},t)$, as $N_j(t) = \int_V \mathrm{d}^3 r|\phi_j(\boldsymbol{r},t)|^2 = \int_V \mathrm{d}^3 r n_j(\boldsymbol{r},t)$.

3. Results and discussions

Simple metal clusters made out of alkaline atoms always serve as a prototype for generic studies due to a single-valence s-electron per atom being fully delocalized over the whole system. Na_2 is the simplest cluster in alkaline metal clusters. Thus we choose Na_2 as an example for examining the validity of the TDLDA model.

Our calculations are performed for a two-colour laser field with intensity $I_1 = 6 \times 10^{12}$ W/cm^2 at $\lambda_1 =$ 1064 nm($\omega = 1.165$ eV) and $I_2 = 1.5 \times 10^{12}$ W/cm^2 at $\lambda_2 = 532$ nm ($2\omega = 2.33$ eV). Figure 1(a) gives the electric field of one-colour laser field with $\omega =$ 1.165 eV. Figure 1(b) illustrates the electric field of the $\omega + 2\omega$ coherent superpositions. There are similar pulse profiles and local maxima and minima of equal absolute amplitude strength in Figs.1(a) and 1(b). The only difference of them is that one only has ω component and the other has ω and 2ω components. In the following, we show the response of Na_2 to one-colour and two-colour laser fields.

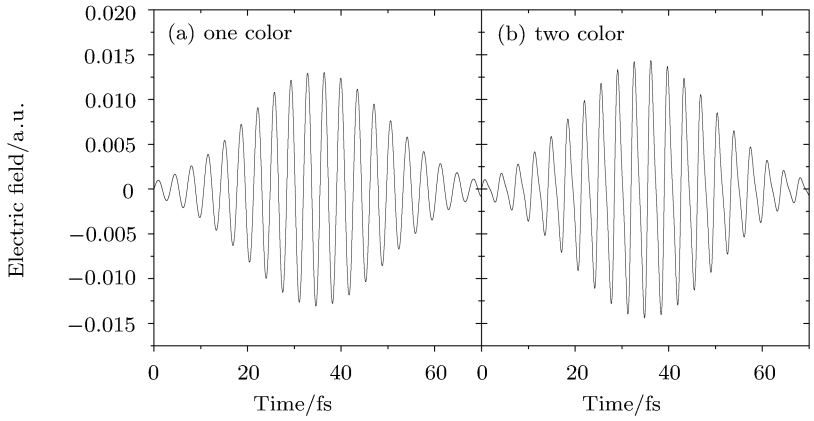


Fig.1. Electric field for a one-colour 25-fs laser pulse: $\lambda = 1064$ nm, $I = 6 \times 10^{12}$ W/cm^2. (b) same as (a) but for two-colour: $\lambda_1 = 1064$ nm, $\lambda_2 = 532$nm, $I_1 = 6 \times 10^{12}$ W/cm^2, $I_2 = I_1/4$, and relative phase $\phi = 0$.

In Fig.2(a), we show the changes of dipole moments of Na_2 along x, y and z directions (x direction is defined as the direction of the symmetry axis connecting two atoms of Na_2, y and z directions as the other two directions orthogonal to the symmetry axis) respectively, obtained with TDLDA for a one-colour laser field at $\lambda = 1064$ nm, $I = 6 \times 10^{12}$ W/cm^2, and pulse duration 25 fs. Figure 2(c) is the same as Fig.2(a) but is for a two-colour ($\omega + 2\omega$) coherent superposition laser field $E(t)$, see Eq.(1). Figures 1(a) and 1(c) show that the changes of dipole moment of Na_2 along x direction are distinct while those along y and z are very small, due to laser polarization direction being along x direction. By the Fourier transform of dipole moments, HHG spectra can be obtained, see Eqs.(9) and (10). Figures 2(b) and 2(d) give HHG spectra for Na_2 from our TDLDA calculations in one-colour and two-colour laser fields, respectively. As we know, the chosen laser intensities and wavelengths determine certain essential physical parameters which allow for quasistatic interpretations of strong field laser-atom processes.[22,23] In this paper, ponderomotive energy $U_p = eI/4m\omega^2$ for $\omega = 1.165$ eV and $2\omega = 2.33$ eV are 0.56 eV and 0.035 eV respectively. The Keldysh parameter γ separating tunnelling and multiphoton ionization regimes for Na_2 ionization potential $I_p = 5.0199$ eV is $\gamma = \sqrt{I_p/2U_p} = 2.1$ so that the present parameters situate our calculations above the tunnelling ionization regime. In this regime, considering ionization as direct transition, we identify the minimal photon number n_s for Na_2 ionization, which is given by $n_s = I_p/\omega = 4$. According to the quasiclassical model, the cutoff of HHG is at $E_{max} = I_p + 3.17U_p$, which corresponds to harmonic order 7 for Na_2. From Figs.2(b) and 2(d), we can see that the distinct Mie plasmons peak presents in the position (2.02 eV), i.e., between the first and the second harmonics, which is consistent with experimental value. The HHG spectra in Fig.2 show hardly any indication for plateaus beyond the second harmonic, but instead decrease more or less continuously. This result is different from that of atoms or other molecules which have the large extent of HHG plateaus. The main reason is the tails of Mie plasmons absorb most of the oscillator strength beyond the second harmonic so that the HHG cutoff is reset.

From Figs.2(b) and 2(d), we can also see that the obvious second order harmonic presents for two-colour excitation while that does not show for one-colour. A possible physical reason is that second har-

monic generation requires broken reflection symmetry because only this allows that second harmonic generation transforms a squared dipole excitation into one dipole signal, i.e., $\hat{D}^2 \longrightarrow \hat{D}$. That transition cannot be mediated by a reflection symmetric system because parity is then conserved, but $\hat{D}$ has negative parity while $\hat{D}^2$ has positive parity. Free Na_2 is too symmetric and closes to spherical, since only s states are occupied, which can be seen also from the dipole moment $d_x(0) = d_y(0) = d_z(0)$. A two-colour laser field breaks the symmetry of Na_2 so that there is a second harmonic signal. An alternative explanation is that even harmonic results from the sum of an odd number of 2ω photons plus two 1ω photons. As far as the generation of even harmonic in two-colour fields is concerned, further investigation is necessary.

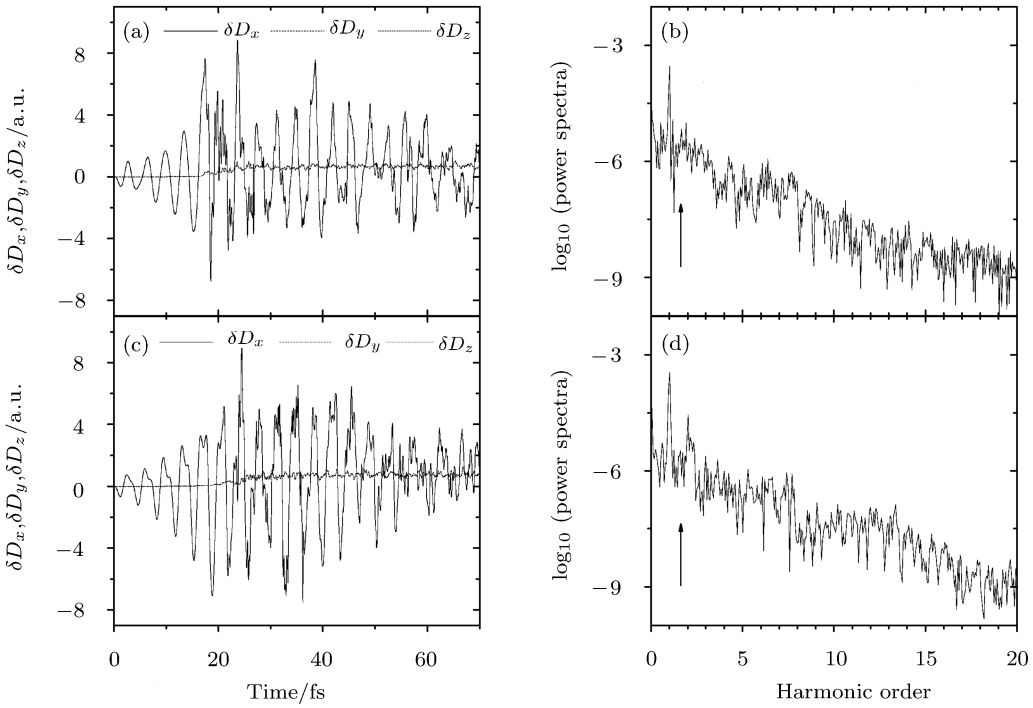


Fig.2. (a) The changes of dipole moments along x, y and z directions for Na_2 in a one-colour laser field, defining x direction as the direction of the symmetry axis connecting two atoms of Na_2; (b) HHG spectra for Na_2 in a one-colour laser field, the arrow indicates the position for the Mie plasmon energy; (c) same as (a) but for a two-colour laser field; (d) same as (b) but for a two-colour laser field.

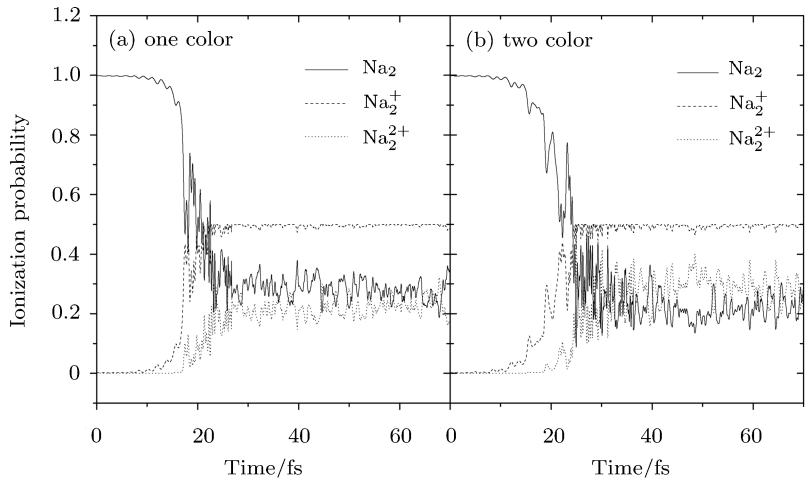


Fig.3. The ionization probabilities of various charge states of Na_2 in a one-colour laser field; (b) same as (a) but for a two-colour field.

The ionization probabilities of various charge states for Na_2 in one-colour and two-colour laser fields are shown in Figs.3(a) and 3(b) respectively. Comparing them, we can see that there is mainly neutral Na_2 cluster and the probabilities of Na_2^+ and Na_2^{2+} almost are zero for one-colour and two-colour laser fields, before 10 fs. While the changes of ionization probabilities are different for one-colour and two-colour laser fields in the 10–25 fs range. During this range, the probability of Na_2^+ increases slowly before 16 fs while increase steeply after 16 fs for one-colour; while it increases step by step for two-colour. The probability of Na_2^+ is about 0.5 at 21 fs for one-colour while it increases to 0.5 at 25 fs for two-colour. After 25 fs, the changes of the probability of Na_2^+ are very small for both one-colour and two-colour. After 25 fs, there is competence of Na_2 and Na_2^{2+}. For one-colour, the probability of Na_2^{2+} is slightly smaller than that of Na_2; for two-colour, on average, the probability of Na_2 is the same as that of Na_2^{2+}. We can say that the probability of higher charge state is larger for two-colour than that for one-colour. This is because local maximum of amplitude strength for two-colour is larger than that for one-colour. This is consistent with the result from the interaction of atoms and laser fields.[24]

From the above results, one can find that the present TDLDA model is capable of correctly describing the HHG and multiphoton ionization of small cluster systems in the multiphoton ranges.

4. Summary

In this paper, we have simulated the HHG spectra and ionization of Na_2 induced by one-colour and two-colour laser fields in the multiphoton regimes with TDLDA. It is shown that a two-colour laser field can result in the breaking of the symmetry and generate the even order harmonic such as the second order harmonic. Two-colour laser field can increase the ionization probability of higher charge state. One can also see that the HHG spectra of Na_2 show hardly any indication for plateaus beyond the second harmonic. In a metal cluster, valence electrons are much more weakly bound, and are delocalized over the entire ionic background, with a high density of states. Thus, the electron dynamics exhibits pronounced collective or plasmon effects. As a consequence, HHG spectra of Na_2 have no large extent of plateaus.

In the future, we will combine the electron dynamics with the ion dynamics within the frame of TDDFT to calculate dissociation process, the kinetic spectra of emitted electrons or fragments, the angular distribution of above threshold ionization electrons and so on.

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