Laser-induced processes with homonuclear diatomic molecules in orthogonally polarized two-color laser field

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Abstract. Using our theory which is based on the strong-field approximation we analyze high-order above-threshold ionization and high-order harmonic generation processes for the case of the homonuclear diatomic molecules exposed to an orthogonally polarized two-color (OTC) laser field. The OTC field represents a superposition of two linearly polarized fields with mutually orthogonal polarizations and different frequencies. We analyze the photoelectron energy spectra and the harmonic ellipticity as a function of the ratio of the intensities of the OTC laser-field components and the relative phase. Some combinations of the values of these parameters lead to the high-energy electrons, while the harmonic ellipticity depends strongly on the ratio of the intensities of the laser-field components. It is possible to find the value of this ratio for which the ellipticity of the emitted harmonics is large. The signs of ellipticity are opposite for the molecular orientations which are connected through the reflection with respect to the axis along the first OTC field component. This symmetry is explained using the expression which relates the $T$-matrix element and the harmonic ellipticity.

1. Introduction
During the past four decades the laser-induced processes have attracted a lot of attention. To observe these processes we need a strong laser field with the intensity of the order $10^{12} - 10^{14}$ W/cm². Two of these processes, high-order above-threshold ionization (HATI) and high-order harmonic generation (HHG) are particularly important. We can use the three-step model [1, 2] to explain intuitively the underlying physics. In the first step the electron is ionized under the influence of the laser field. In the second step, the electron propagates in the combined potential of the laser field and the parent ion. If the laser field is strong enough, the influence of the parent ion can be neglected. The situation where ionized electron goes directly to the detector corresponds to the so-called above-threshold ionization (ATI) process [3] and these electrons are usually referred as direct electrons. However, the oscillatory character of the laser field can bring the electron back in the vicinity of the parent ion. Then the electron can rescatter elastically of the parent ion or recombine with it emitting a high-energy photon. The
first scenario corresponds to the HATI, and the second one to the HHG process. The rescattered electrons can obtain much higher energies than the direct electrons. The energy of the emitted high-order harmonic is equal to the integer multiple of the laser-field photon energy. For a broad energy interval the photoelectron (HATI) or photon (HHG) yield is practically constant. This interval is called the plateau of the spectrum. This plateau finishes with an abrupt cutoff, after which the yield is practically zero.

When the molecular target is used instead of the atomic target, additional parameters have to be taken into account. Particularly important parameters are the internuclear distance and the angles which determine the molecular orientation in the laser field. The symmetry of the molecular orbital has to be taken into account as well. Many interesting features can be observed in the molecular HATI and HHG spectra. For example, the double-slit and multiple-slit interference effects were observed in the HHG spectra [4, 5, 6, 7], and in the HATI spectra [8, 9, 10]. In addition, if the so-called tailored laser field is used instead of a linearly polarized field, many new phenomena can be observed. For example, the harmonics produced using linearly polarized laser field and atomic targets are linearly polarized. However, when atom is exposed to the tailored laser field, which consists of two or more components with different frequencies and polarizations, significantly different harmonic polarizations may be expected. The elliptically polarized light is important for various applications, such as investigation of magnetic structure of materials, or study of the chiral properties of organic molecules [11]. That is why it is very desirable to have table top schemes for the production of the high-frequency elliptically polarized light [12].

In this paper, we analyze the HATI and HHG processes using the orthogonally polarized two-color (OTC) laser field. This field consists of two linearly polarized laser fields with frequencies \(r\omega\) and \(s\omega\) (\(r\) and \(s\) are integers and \(\omega\) is the fundamental frequency) and mutually orthogonal polarizations. We are particularly interested in the combinations having the frequency ratios 1 : 2 and 1 : 3. The symmetries in the HATI spectrum, obtained using homonuclear diatomic molecules exposed to a strong OTC laser field were analysed in [13]. These symmetries are a consequence of the symmetries of the system consisting of a homonuclear diatomic molecule and an OTC laser field. In [14] we analysed the emission rate and ellipticity of the emitted harmonics generated by the exposure of a diatomic homonuclear molecule to a strong OTC laser field. Now we want to analyze how the ratio of the intensities of the laser field components and the relative phase can be used to control the HATI and HHG yields. Since the calculations based on the time-dependent Schrödinger equation are time-demanding even for the simplest molecules, we use the theory based on the strong-field approximation (SFA). In the SFA theory, the interaction of the ionized electron with the parent ion is neglected during the electron propagation before the rescattering or recombination.

This paper consists of four sections. In Section 2 we briefly present the theory based on the SFA for neutral homonuclear diatomic molecules in the OTC laser field. The obtained numerical results are presented in Section 3, while the conclusions and discussions are given in Section 4. We use the atomic system of units (\(\hbar = e = m_e = 4\pi\varepsilon_0 = 1\)).

2. Theory

The theory of strong-field ionization of diatomic molecules is presented in [15], further developed in [8, 5] and applied to the OTC laser field in [13, 14]. The diatomic molecule is modelled as a three-particle system consisting of two heavy atomic centers and one electron. The OTC laser-field vector is given by

\[
E(t) = E_1 \sin(r\omega t)\hat{e}_{Lx} + E_2 \sin(s\omega t + \varphi)\hat{e}_{Lx},
\]

where \(I_j = E_j^2, j = 1, 2\), are the intensities of the laser-field components and \(\varphi\) is the relative phase. The laser field and molecule are in the same plane and the position of the molecule
relative to the laser field is determined using the angle $\theta_L$ between the internuclear axis and the axis along the unit vector $\hat{e}_z$.

First, we briefly present the theory of the molecular HATI. The differential ionization rate for the emission of an electron with the final momentum $\mathbf{p}$ and energy $E_p = p^2/2$ is

$$w_{R_p}(n) = 2\pi p|T_{R_p}(n)|^2,$$

where $R$ is the equilibrium internuclear distance and $i$ stands for the initial molecular state. The $T$-matrix element $T_{R_p}(n)$ can be written as

$$T_{R_p}(n) = \frac{1}{T} \int_0^T df_{R_p}(t)e^{i[Tf(t)+n\omega t]},$$

where $U(t) = p \cdot \alpha(t) + \int^t dt' A^2(t')/2 - U_p t$ and $f_{R_p}(t) = f_{R_p}^{(0)}(t) + f_{R_p}^{(1)}(t)$, with $f_{R_p}^{(0)}(t)$ ($f_{R_p}^{(1)}(t)$) corresponding to the direct (rescattered) electrons. Here $U_p = I_1/(2r\omega)^2 + I_2/(2s\omega)^2$ is the ponderomotive energy and $\alpha(t) = \int dt A(t)$, where the vector potential is $A(t) = -\int dt E(t)$. These contributions are [16]

$$f_{R_p}^{(0)}(t) = \sum_{q,a} c_{qa} e^{iqpR/2} \langle p + A(t)|E(t)\cdot r|\psi_a \rangle,$$

$$f_{R_p}^{(1)}(t) = -ie^{-iS_{st}(t)} \int_0^\infty d\tau \frac{(2\pi i)^{3/2}}{\tau} e^{i[S_{st}(t')-I_p\tau]} \sum_{q'=\pm 1} V_{eK}^{q'} e^{-iq'K \cdot R/2} \sum_{a} c_{qa} e^{iqk \cdot R}|\psi_a\rangle.$$

The molecular orbital of the initial state $i$ is given by a linear combination of the Slater-type atomic orbitals $|\psi_a\rangle$, the sum over $q$ is the sum over the atomic centers, $I_p$ is the ionization potential, $t'(t)$ is the time of ionization (recombination), $\tau = t - t'$ is the so-called travel time, $K = k_{st} - p$, $k_{st} = -\int_0^\infty dt'' A(t'')/\tau$ is the stationary electron momentum, $S_{st}(t) = \int_0^t dt'' |k_{st} + A(t'')|^2/2$, and $V_{eK}^{q'}$ is the Fourier transform of the rescattering potential at the corresponding atomic center $q'$. We now present the theory of the molecular HHG. The complex vector which corresponds to the $T$-matrix element for the emission of the photon having frequency $n\omega$, wave vector $K$, and the polarization $\hat{e}_n$ is [5]

$$T_n = -i \left(\frac{2\pi}{i}\right)^{3/2} \int_0^T \frac{dt}{T} e^{in\omega t} \int_0^\infty \frac{d\tau}{\tau^{3/2}} \sum_{q=\pm 1} \sum_{a} c_{qa} e^{-iqk_{st} \cdot A(t)} e^{iR/2} m_a(k_{st}, t) \times e^{iS(k_{st}, t', t')} \sum_{q'=\pm 1} \sum_{a'} c_{q'a'} e^{iq'k_{st} \cdot R/2} m_{a'}(k_{st}, t') \cdot E(t'),$$

where $T = 2\pi/\omega$ is the period of the laser field, $S(k_{st}; t, t') = -\int_0^t dt'' ([k_{st} + A(t'')]^2/2 + I_p)$ is the action, and $m_a(k_{st}, t) = \langle \psi_a \mid r \mid k_{st} + A(t) \rangle$ is the dipole matrix element. The harmonic emission rate is given by

$$w_n = \frac{1}{2\pi} \left(\frac{n\omega}{c}\right)^3 |T_n|^2.$$
Using the numerically calculated components $T_z = T_n \cdot \hat{e}_L z$ and $T_x = T_n \cdot \hat{e}_L x$, we calculate the harmonic ellipticity by the relation [17]

$$\varepsilon_n = \text{sgn}(\xi_n) \left( \frac{1 - \sqrt{1 - \xi_n^2}}{1 + \sqrt{1 - \xi_n^2}} \right)^{1/2},$$

where the degree of circular polarization is

$$\xi_n = \frac{\text{Im}[2(T_x^* T_x)]}{|T_n|^2}.$$  \hfill (9)

3. Numerical results

In this section we present the photoelectron energy spectra and high-order harmonic spectra obtained using an orthogonally polarized two-color laser field. We analyze the photoelectron energy and the differential ionization rate as functions of the ratio of the intensities of the laser-field components and the relative phase for $\omega - 2\omega$ and $\omega - 3\omega$ OTC laser fields. We also calculate the ellipticity of the emitted harmonics for various ratios of the intensities of the laser-field components. We use the O$_2$ and N$_2$ molecules as examples. For the O$_2$ (N$_2$) molecule, the highest occupied molecular orbital (HOMO) is $1\pi_g$ ($3\sigma_g$). The equilibrium internuclear distance and the ionization potential for O$_2$ are $R = 2.282$ a.u. and $I_p = 12.3$ eV, respectively, while these quantities are $R = 2.068$ a.u. and $I_p = 15.58$ eV for N$_2$. The molecular orbital is modelled using the Slater-type orbitals. For the O$_2$ molecule, five atomic orbitals are taken into account: three $p$, one $d$ and one $f$ orbital. The HOMO of the N$_2$ molecule is modelled using 12 atomic orbitals: five $s$, three $p$, three $d$ and one $f$ orbital.

3.1. Photoelectron energy spectra

![Figure 1](image-url)

Figure 1. Logarithm of the differential ionization rate of the O$_2$ molecule presented in false colors as a function of the photoelectron energy and ratio of the intensities of the laser-field components. The intensity and the wavelength of the first OTC field component are $I_1 = 4 \times 10^{13}$ W/cm$^2$ and $\lambda = 1300$ nm, respectively, while the relative phase is $\varphi = 90^\circ$. The molecular orientation angle is $\theta_L = 60^\circ$. The left (right) panel corresponds to the $\omega - 2\omega$ ($\omega - 3\omega$) OTC laser field.

We have found that the high-energy photoelectron spectra depend strongly on the relative phase between the laser-field components [13]. Now we want to analyze how the photoelectron
spectra depends on the ratio of the intensities of the laser-field components. In figure 1 we present the logarithm of the differential ionization rate of the $O_2$ molecule as a function of the photoelectron energy and the ratio of the intensities of the laser-field components. The intensity and the wavelength of the first OTC field component are $I_1 = 4 \times 10^{13}$ W/cm$^2$ and $\lambda = 1300$ nm, respectively, while the relative phase is $\varphi = 90^\circ$. The molecular orientation angle is $\theta_L = 60^\circ$. The left (right) panel corresponds to the $\omega-2\omega$ ($\omega-3\omega$) OTC laser field. It is clear that the photoelectron spectra depend strongly on the ratio of the intensities of the laser-field components. For some photoelectron energies and some values of the ratio $I_2/I_1$, the differential ionization rate is low. For example, in the photoelectron spectrum obtained using the $\omega-2\omega$ OTC laser field, the differential ionization rate for the emission of electrons with energies close to $7U_p$ is low for a broad range of the values of the ratio $I_2/I_1$. For the $\omega-3\omega$ OTC laser field, the electrons with the highest energy can be expected when the laser-field components have the same intensity. In addition, the photoelectron spectrum depends strongly on the relative phase between the laser-field components. In figure 2 we present the logarithm of the differential ionization rate of the $O_2$ molecule as a function of the relative phase and the photoelectron energy for the same parameters as in figure 1. The intensity of the laser-field component having the frequency $s\omega$ is $I_2 = 0.75I_1$. The results shown in the left (right) panel are obtained using the $\omega-2\omega$ ($\omega-3\omega$) OTC laser field. For the $\omega-2\omega$ ($\omega-3\omega$) OTC laser field, the electrons with the highest energy can be expected for the relative phase around $\varphi = 30^\circ$ ($\varphi = 80^\circ$). For these relative phases it is possible to further analyze the dependence on the ratio $I_2/I_1$. The results are similar to those presented in figure 1. According to the presented results, we conclude that the ratio $I_2/I_1$ and the relative phase can be used as control parameters. The optimal conditions which lead to the photoelectrons having the highest energy can be assessed in the following way. First, one finds the ratio $I_2/I_1$ which corresponds to the high-energy electrons for an arbitrary relative phase. Then, for this ratio one calculates the spectra for different relative phases between the laser-field components and finds the value of $\varphi$ which leads to the highest photoelectron energy. Finally, it is necessary to check the behaviour of the photoelectron spectra calculated with the obtained relative phase for different values of the ratio $I_2/I_1$.

Figure 2. Logarithm of the differential ionization rate of the $O_2$ molecule presented in false colors as a function of the photoelectron energy and relative phase between the laser-field components. The intensity of the laser-field component with the frequency $s\omega$ is $I_2 = 0.75I_1$, while the other parameters are the same as in figure 1. The left (right) panel corresponds to the $\omega-2\omega$ ($\omega-3\omega$) OTC laser field.
3.2. Ellipticity of high-order harmonics

Figure 3. The ellipticity of the emitted harmonics in the HHG process obtained by exposing the N$_2$ molecule to the $\omega$–2$\omega$ OTC laser field, as a function of the harmonic order for different ratios $I_2/I_1$. The intensity and the wavelength of the first OTC field component are $I_1 = 7 \times 10^{13}$ W/cm$^2$ and $\lambda = 2000$ nm, respectively, while the relative phase is $\varphi = 50^\circ$. The molecular orientation angle is $\theta_L = 45^\circ$. The left (right) panel corresponds to the odd (even) harmonics.

Figure 4. The ellipticity of the emitted harmonics in the HHG process obtained by exposing the N$_2$ molecule to the $\omega$–2$\omega$ OTC laser field, as a function of the harmonic order for molecular orientations $\theta_L = 45^\circ$ (black curve) and $-\theta_L$ (red curve). The intensity of the laser-field component with the frequency $s\omega$ is $I_2 = 0.75I_1$, while the other laser-field parameters are the same as in figure 3. The left (right) panel corresponds to the odd (even) harmonics. The intensity of the laser-field components influences the components of the
$T$-matrix element and, as a consequence, the degree of circular polarization and the harmonic ellipticity. For example, the ellipticity of the high-energy odd harmonics increases with the increase of the ratio $I_2/I_1$. This behaviour is also present for the even harmonics, but it is less pronounced. Generally, the elliptically polarized harmonics can be obtained using the molecular targets and the OTC laser field, and the ellipticity can be controlled using the ratio of the intensities of the laser-field components as a control parameter.

It is also interesting to note that the signs of ellipticity are opposite for the molecular orientations $\theta_L$ and $-\theta_L$. This is illustrated in figure 4, where we present the harmonic ellipticity as a function of the harmonic order for the molecular orientations $\theta_L = 45^\circ$ (black curves) and $-\theta_L$ (red curves), and for odd (left panel) and even (right panel) harmonics. The intensity of the laser-field component with the frequency $s\omega$ is $I_2 = 0.75I_1$, while the other laser-field parameters are the same as in figure 3.

This symmetry is exact and can be explained using the relations (6), (8) and (9). The transformation $\theta_L \rightarrow -\theta_L$ results in one component ($T_z$ or $T_x$) of the $T$-matrix element changing its sign. As a consequence, the degree of circular polarization and the harmonic ellipticity also change the sign.

4. Conclusions
We have analysed high-order above-threshold ionization and high-order harmonic generation spectra obtained exposing homonuclear diatomic molecular targets to an orthogonally polarized two-color laser field. We have found that the ratio of the intensities of the laser-field components and the relative phase can be used as control parameters. For some combinations of these parameters, the high-energy electrons are emitted. In order to find these combinations, it is necessary to find the optimal ratio of the intensities which corresponds to the photoelectrons with the highest energy. For this ratio, we calculate the spectra for different relative phases between the laser-field components, and find the optimal value of the relative phase. Finally, it is necessary to check the behaviour of the photoelectron spectra calculated with the obtained optimal relative phase for different values of the intensity ratio. In this way, it is possible to assess the values of the relative phase and the ratio of the intensities of the laser-field components for which the high-energy electrons can be expected.

We also analysed the ellipticity of the emitted harmonics, obtained by the OTC laser field, as a function of the ratio of the intensities of the laser-field components. We have found that the ellipticity of the emitted harmonics can be large for some values of this ratio. It is particularly important that the regions corresponding to a large ellipticity are also in the high-energy part of the spectrum, so that the molecular HHG obtained using the OTC field can be used as a source of the high-frequency elliptically polarized light. Finally, we analysed the ellipticity of the emitted harmonics for the molecular orientations which are connected through the reflection with respect to the axis along the first OTC field component. The ellipticity signs of the emitted harmonics are opposite for these molecular orientations. This behaviour is a consequence of the transformation rule of the $T$-matrix element when the molecular orientation angle $\theta_L$ changes the sign and the connection (9) of the ellipticity and the $T$-matrix element.

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