PHYSICAL REVIEW A **75**, 032518 (2007)

# Photoinduced electric currents in ring-shaped molecules by circularly polarized laser pulses

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(Received 2 December 2006; published 26 March 2007)

We have theoretically demonstrated that circularly polarized laser pulses induce electric currents and magnetic moments in ring-shaped molecules $\mathrm{Na}_{10}$ and benzene. The time-dependent adiabatic local density approximation is employed for this purpose, solving the time-dependent Kohn-Sham equation in real space and real time. It has been found that the electric currents are induced efficiently and persist continuously even after the laser pulses were switched off provided the frequency of the applied laser pulse is in tune with the excitation energy of the electronic excited state with the dipole strength for each molecular system. The electric currents are definitely revealed to be a second-order nonlinear optical response to the magnitude of the electric field. The magnetic dipole moments inevitably accompany the ring currents, so that the molecules are magnetized. The production of the electric currents and the magnetic moments in the present procedure is found to be much more efficient than that utilizing static magnetic fields.

DOI: 10.1103/PhysRevA.75.032518 PACS number(s): 33.15.Kr, 36.40.Vz, 42.65.−k, 73.23.Ra

## I. INTRODUCTION

Production and dynamics of electric and spin currents in semiconductor nanostructures or mesoscopic systems have been receiving much attention over the years [1–4]. This is because such electron dynamics in correlated electron systems is one of the most important issues to be settled in condensed matter physics. Furthermore, control of these currents is crucial to develop quantum devices in material science. The details of the electronic conduction have considerably been studied mainly in bulk or mesoscopic systems, whereas the electric or spin currents in molecules are also of increasing importance in the context of molecular-sized electronic devices based on advanced fabrication technologies. For example, molecular junctions have already been realized and quantum transport properties of the electrons at the junctions have being investigated intensively [5]. The electric or spin currents are in general driven by a bias voltage or spin injection in the systems interacting with contacts. These biased systems are, however, not necessarily ideal in elucidating the electron dynamics and in controlling the currents.

Recently, some groups theoretically proposed that the application of coherent laser pulses induces electric currents or spin-polarized currents much more directly in model systems of ballistic rings or semiconductors in the absence of a bias (i.e., no contacts were required) [6–8]. The idea of the photoinduced electric and spin currents has great advantages because the laser pulses allow ultrafast and coherent control of the currents without any dissipation. However, the previous theoretical studies have been performed only in rather simple model systems in which neither electron-electron nor electron-ion interaction is taken into account. Although these model studies might be useful to understand the phenomena qualitatively, the electron-electron and electron-ion interaction should have a great influence on the electron dynamics. We thus think that it is highly desirable to carry out first-principles calculations of the photoinduced electric currents in real molecular systems and to elucidate the mechanisms of their production.

In the present study, we consider two planar ring-shaped molecules, $\mathrm{Na}_{10}$ and benzene. The $\mathrm{Na}_{10}$ molecule will be an ideal system to understand the mechanism of producing the electric currents in the ring-shapes molecule, although the fabrication of such a cluster in a stable form would not be easy. We describe the electron dynamics in these molecules induced by circularly polarized pulse laser fields in the time-dependent density functional theory (TDDFT) with adiabatic and local density approximations.

This paper is organized as follows. In Sec. II, our numerical approach based on TDDFT is described. In Sec. III, we show the numerical results of the photoinduced electric currents and investigate mechanisms of the current formation. In particular, we demonstrate that the electric currents are formed as a second-order nonlinear optical response. We also propose an experimental design to measure the photoinduced electric currents considered in this article. Concluding remarks are given in Sec. IV.

## II. COMPUTATIONAL PROCEDURE

We describe the electron dynamics of the photoinduced electric currents with TDDFT [9]. In TDDFT, the time evolution of the density and the current of an interacting $N$-electron system is described by the time-dependent Kohn-Sham (TDKS) equation for auxiliary electronic wave functions $\psi_j(\mathbf{r},t)$ [10–12],

$$i\hbar\frac{\partial}{\partial t}\psi_j(\mathbf{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\mathrm{eff}}[\rho](\mathbf{r},t)\right]\psi_j(\mathbf{r},t), \qquad (1)$$

where $m$ is the electron mass and $\rho$ is the electron density given by

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$$\rho(\mathbf{r},t) = 2\sum_{j=1}^{N/2} |\psi_j(\mathbf{r},t)|^2. \tag{2}$$

The factor of 2 indicates that each Kohn-Sham (KS) orbital is fully occupied (i.e., a closed shell system). The effective potential $V_{\mathrm{eff}}[\rho](\mathbf{r},t)$ is a functional of $\rho$, and it consists of four terms of an ion-electron interaction potential $v_{\mathrm{ion}}(\mathbf{r})$, a time-dependent Hartree potential, an exchange-correlation (XC) potential $v_{\mathrm{xc}}[\rho](\mathbf{r},t)$, and an external potential of a laser field $v_{\mathrm{laser}}(\mathbf{r},t)$ as follows:

$$V_{\mathrm{eff}}[\rho](\mathbf{r},t) = v_{\mathrm{ion}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\mathrm{xc}}[\rho](\mathbf{r},t) + v_{\mathrm{laser}}(\mathbf{r},t). \tag{3}$$

We use norm-conserving pseudopotentials for the ion-electron interaction $v_{\mathrm{ion}}(\mathbf{r})$ of each atomic (Na, C, H) component [13,14]. One electron ($3s$) for Na and four electrons ($2s^2 2p^2$) for C are explicitly treated, whereas the other core electrons are frozen. Therefore, we numerically solve 10-electron dynamics for $\mathrm{Na}_{10}$ and 30-electron dynamics for benzene.

For the XC potential, we use the following adiabatic local density approximation (ALDA):

$$v_{\mathrm{xc}}[\rho](\mathbf{r},t) \approx v_{\mathrm{xc}}^{\mathrm{ALDA}}[\rho](\mathbf{r},t) = v_{\mathrm{xc}}^{\mathrm{LDA}}[\rho_0](\mathbf{r})\big|_{\rho_0(\mathbf{r})=\rho(\mathbf{r},t)}, \tag{4}$$

where $v_{\mathrm{xc}}^{\mathrm{LDA}}[\rho_0](\mathbf{r})$ is the ground state LDA XC potential. We adopt the one given by Perdew and Zunger [15]. In ALDA, the XC potential at $\mathbf{r}$ and $t$ is approximated by that of the ground state uniform electron gas having the density $\rho(\mathbf{r},t)$, ignoring the nonlocality in both $\mathbf{r}$ and $t$. Despite its simplicity, ALDA has practically provided reasonable results for single-electron excitations well below the lowest ionization threshold of systems [16–18]. In the present study, we are also interested in the lowest single-electron excitations well below the first ionization threshold. Recently, there are extensive efforts to develop more accurate exchange-correlation functionals including the current density functionals [19–22]. However, these functionals have not yet been verified sufficiently.

As the external potential $v_{\mathrm{laser}}(\mathbf{r},t)$ representing the circularly polarized laser pulse, we take the following form of

$$v_{\mathrm{laser}}(\mathbf{r},t) = exE\sin^2\left(\frac{\pi t}{T}\right)\cos\omega t \pm eyE\sin^2\left(\frac{\pi t}{T}\right)\sin\omega t$$

$$(0 < t < T), \tag{5}$$

where $e$ is the electric charge, $E$ is the field strength, $\omega$ is the laser frequency, and $T$ determines the laser pulse duration. The signs of $\pm$ indicate either the right- or left-handed circularly polarized laser pulse. A laser intensity is related to the field strength by $I=\frac{1}{2}\epsilon_0 cE^2$, where $\epsilon_0$ is the permittivity of free space and $c$ is the speed of light. The laser pulse profile is chosen as $\sin^2(\frac{\pi t}{T})$ in which five-cycle (for $\mathrm{Na}_{10}$) or ten-cycle (for benzene) electric fields are included.

The TDKS equation (1) is solved numerically by a grid-based method in three-dimensional Cartesian coordinates [10,11]. The time propagation of the KS orbitals is carried out with a fourth-order Taylor expansion, and the Laplacian operator is evaluated by a nine-point finite difference formula [23]. In the actual calculations, we take constant time steps of 0.001 32 fs for $\mathrm{Na}_{10}$ and of 0.000 99 fs for benzene, and utilize uniform grids with the mesh spacing of 0.6 Å for $\mathrm{Na}_{10}$ and of 0.26 Å for benzene.

The present systems are the planar ring-shaped molecules placed on $xy$ plane. We specify the nearest neighboring Na-Na distance and C-C distance to be 3.34 Å and 1.40 Å, respectively, and the C-H distance to be 1.08 Å. Then, the diameters of the $\mathrm{Na}_{10}$ and $\mathrm{C}_6$ rings are 10.8 Å and 2.79 Å, respectively. In the present calculations, we fix all the nuclear coordinates and focus on the electron dynamics. The time duration is taken up to ~60 fs for $\mathrm{Na}_{10}$ and ~25 fs for benzene. For these time durations, it should be a reasonable approximation to fix the ion positions. In sodium atomic cluster systems subjected to intense laser fields, Calvayrac *et al.* stated that the nuclear motion can be fixed up to ~100 fs [12]. The time duration for benzene (~25 fs) might not be short enough for the hydrogen motion to be frozen because of the lightest atom.

We calculate the time-dependent electric currents by

$$A(t) = 2\sum_{j=1}^{N/2} \frac{\hbar}{2mi}\int_S [(\psi_j^*(\mathbf{r},t)\nabla\psi_j(\mathbf{r},t) - \nabla\psi_j^*(\mathbf{r},t)\psi_j(\mathbf{r},t)]dS, \tag{6}$$

where $S$ is a surface region surrounding a volume that includes a part of the molecule. In the actual calculations, we set the volume to be a semicircular region $(x>0, y>0)$ of the molecular rings. The calculated time-dependent electric current shows rapid oscillation reflecting the oscillating electric field of the employed laser pulse. However, the oscillating current almost cancels after averaging it over a period longer than the laser frequency. To obtain the current that persists even after the average over the laser period, we first define the cumulative number of the electrons passing through the volume from $t=0$ up to $t=\tau$ by

$$\sigma(\tau) = \int_0^\tau A(t)dt. \tag{7}$$

We then define the time-averaged electric currents $\widetilde{A}$ by a linear fitting of the curve $\sigma(\tau)$.

## III. RESULTS AND DISCUSSION

### A. Numerical results for photoinduced electric currents

We first discuss the electric current in $\mathrm{Na}_{10}$, which will be suited to comprehend a mechanism of the photoinduced electric currents in a molecular system. This molecule has an electronic excitation at 1.5 eV with a substantial oscillator strength in the linear response TDDFT. We apply the left-handed circularly polarized laser pulse with a laser frequency $\omega$ in tune with the dipole excitation ($\hbar\omega=1.5$ eV). Figure 1(a) shows the cumulative number of the electrons $\sigma(\tau)$. The laser intensity $I$ is taken to be $1.0\times 10^8$ W/cm$^2$, and the pulse duration $T$ is 13.8 fs. The end of the pulse is indicated

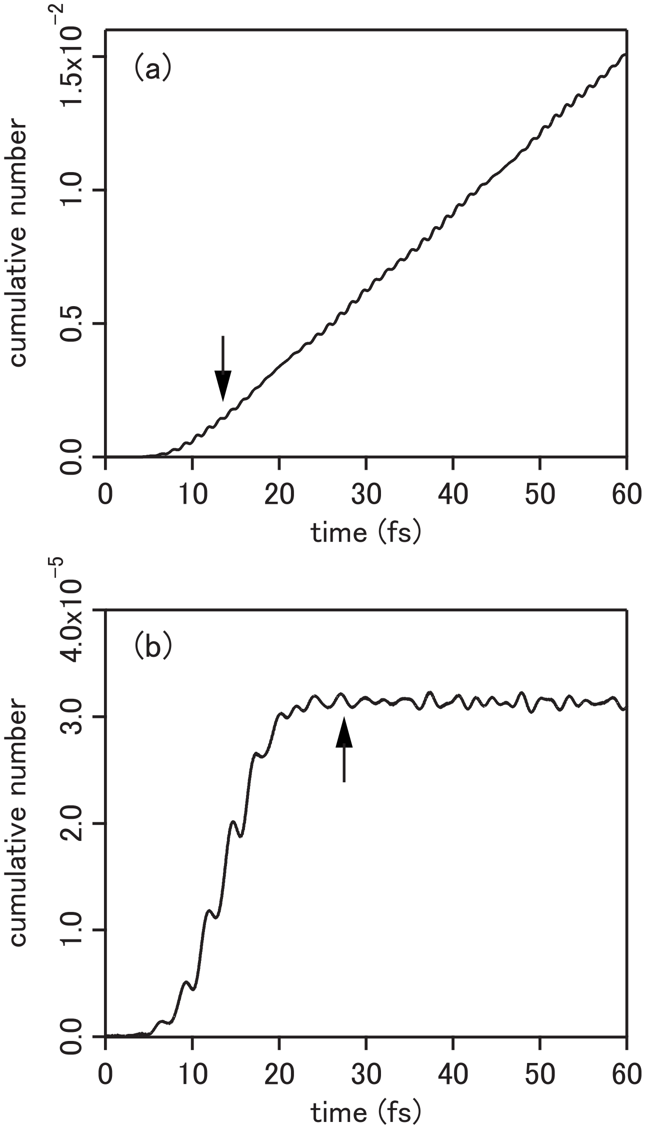

FIG. 1. Cumulative number of the electrons passing through a given volume from $\tau=0$ fs to $\tau=t$ fs in $\mathrm{Na}_{10}$. The applied laser pulses are left-handed circularly polarized and their frequencies are (a) in tune (=1.5 eV) and (b) out of tune (=0.75 eV) with the dipole resonance frequency. The arrows indicate the end of the applied laser pulses; (a) 13.8 fs and (b) 27.6 fs.

by the arrow in the figure. The electron dynamics was further propagated from 13.8 fs up to 60 fs without the external electric field. It is clearly seen from the figure that the cumulative number of the electrons increases almost linearly as a function of time even after the laser pulse was switched off at 13.8 fs. This means that the electrons circulate in the molecular ring steadily and the electric current persists continuously without the external electric fields. The time-averaged electric current is estimated to be ~46.8 nA.

In comparison, we here refer to magnetic-field-induced electric currents. For example, it has been reported both theoretically [24] and experimentally [25] that in ballistic micrometer-sized quantum rings threaded by static magnetic flux (~$10^{-3}$ Tesla), the induced electric currents are in the order of nanoampere. However, the required magnetic flux, which is inversely proportional to the square of the radius of the system, becomes much larger with decreasing the size of the system. If the radius, for example, of a ballistic ring (~$10^{-6}$ m), is shortened to that of a small molecule (~$10^{-9}$ m), the required magnetic flux amounts to 6 orders of magnitude larger than that necessary in the ballistic rings. Since static magnetic field available with the present technology is limited to at most a few tens of Tesla, such huge magnitude of the required magnetic field is not realistic. For this reason, it will not be practical to induce the electric currents in small molecular rings by using the static magnetic field.

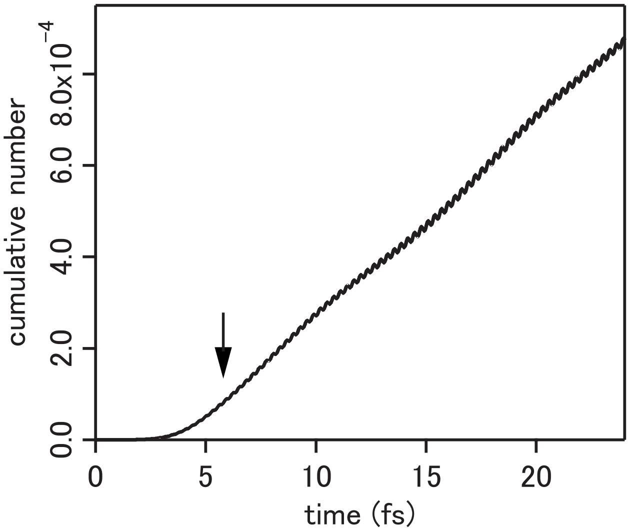

FIG. 2. Same as Fig. 1(a) but in benzene. The applied laser frequency is in tune with the dipole resonance frequency (=6.89 eV). The arrow indicates the end of the applied laser pulse (=6 fs).

Figure 1(b) shows the electric current with the same condition as Fig. 1(a) but the frequency ($\hbar\omega=0.75$ eV) is not in tune with the dipole excitation energy. The laser pulse duration is 27.6 fs. In marked contrast to the on-resonant case, the cumulative number of the electrons becomes constant after the applied laser pulse ends. This apparently means that the electric current is induced only while the laser field is being applied and no current flows without the external electric field. A similar change of the electron dynamics with on- and off-resonant laser frequency has also been studied in the high harmonic generation of the silver clusters by the present authors [26]. Such resonance phenomena are analogous to those in a classical forced oscillator. It should again be noted that $\mathrm{Na}_{10}$ is a rather artificial molecule and might be fabricated on a well-chosen surface. Then, an adsorbate-surface interaction will have an influence on the photoinduced electric current in such a system. However, the mechanism of the electric currents considered here does not change qualitatively.

We next examine the photoinduced electric currents in a more real system. Figure 2 shows the cumulative number of the electrons $\sigma(\tau)$ in benzene when the left-handed circularly polarized laser pulse is applied. The linear response TDDFT calculation well reproduces the electronic excitation of ben-

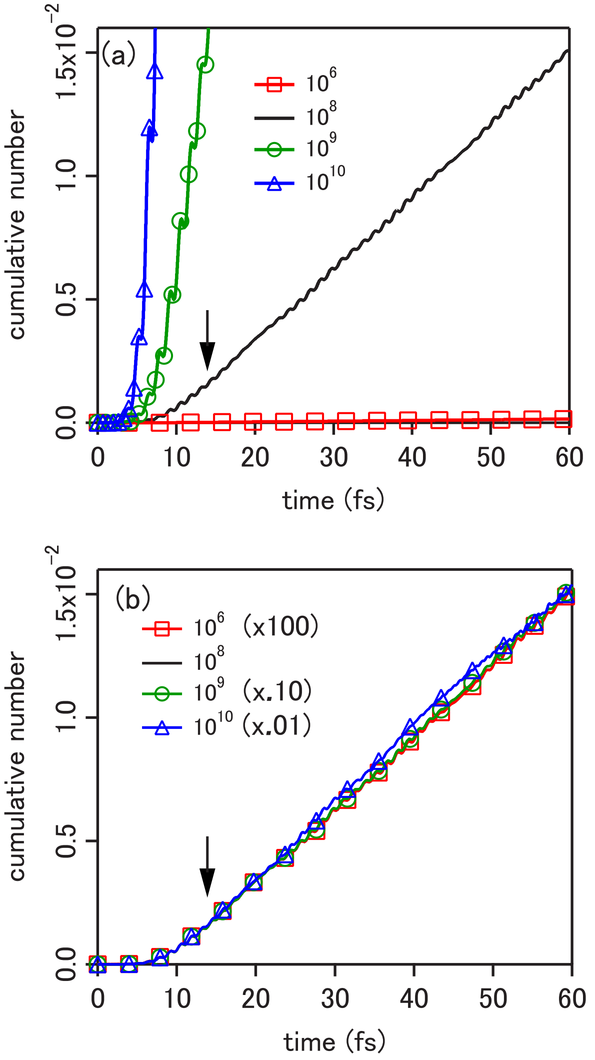

FIG. 3. (Color online) (a) Cumulative number of the electrons in $Na_{10}$ with different laser intensities, $I=1.0\times10^6$ (□), $10^8$ (solid line), $10^9$ (○), $10^{10}$ (△) $W/cm^2$. (b) The curves of $I=1.0\times10^6,10^9,10^{10}$ $W/cm^2$ are multiplied by 100, 1/10, and 1/100, respectively. The arrows indicate the end of the applied laser pulse.

zene with an intense dipole strength at 6.89 eV. The laser frequency is in tune with this excitation energy, $\hbar\omega=6.89$ eV. The laser intensity is $1.0\times10^8$ $W/cm^2$, and the pulse duration is 6 fs. As in the $Na_{10}$ ring, the electric current is induced by the circularly polarized laser pulse and persists continuously even after the laser pulse was switched off at 6 fs (see, the arrow indicated in the figure). The electric current is estimated to be ~7.0 nA. The current in benzene is smaller than that in $Na_{10}$ although the total number of the valence electrons in benzene is larger than that in $Na_{10}$.

To elucidate the mechanism of the photoinduced electric current, we investigate the dependence of the currents on the laser intensity. Figure 3(a) shows the cumulative number of the electrons $\sigma(\tau)$ in $Na_{10}$ with different laser intensities, $I=1.0\times10^6,10^8,10^9,10^{10}$ $W/cm^2$. The applied laser frequency is in tune with the resonance frequency, $\hbar\omega=1.5$ eV. The curve of $I=1.0\times10^8$ $W/cm^2$ is exactly the same as one shown in Fig. 1(a). The figure clearly shows that the photoinduced electric currents strongly depend on the laser intensity. Indeed, the curves for the larger and smaller laser intensities are almost out of range in this scale of the figure. To reveal the effect of the laser intensity, we multiply the $y$ values of each curve of $I=1.0\times10^6,10^9,10^{10}$ $W/cm^2$ by 100, 1/10, and 1/100, respectively. The calculated three curves considerably coincide with the curve of $I=1.0\times10^8$ $W/cm^2$, as clearly shown in Fig. 3(b). [The multiplied red curve (square) of $I=1.0\times10^6$ $W/cm^2$ completely overlaps with the black one (solid line) of $I=1.0\times10^8$ $W/cm^2$.] Since the laser intensity $I$ is proportional to square of the field strength $E$, i.e., $I\propto E^2$, the photoinduced electric currents are considered to be the result of the second-order nonlinear optical response. In other words, the electric currents are induced by the coherent excitation process with the two (i.e., $x$ and $y$ linearly polarized) laser pulses.

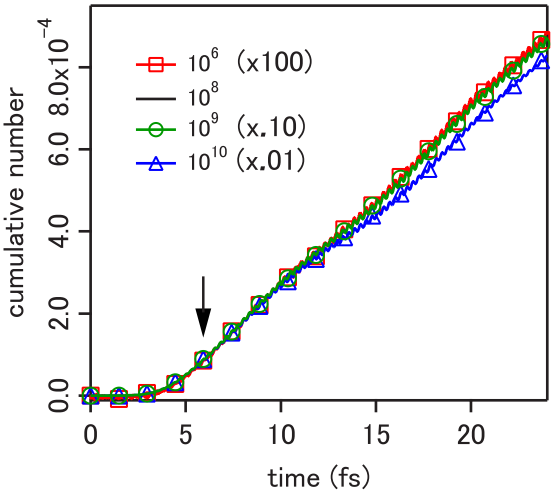

FIG. 4. (Color online) Same as Fig. 3(b) but in benzene.

Figure 4 shows the cumulative number of the electrons $\sigma(\tau)$ in benzene with different laser intensities, $I=1.0\times10^6,10^8,10^9,10^{10}$ $W/cm^2$. The applied laser frequency is in tune with the resonance frequency $\hbar\omega=6.89$ eV. As in the electric currents in $Na_{10}$, the $y$ values of each curve of $I=1.0\times10^6,10^9,10^{10}$ $W/cm^2$ are multiplied by 100, 1/10, and 1/100, respectively, to demonstrate the nonlinear effect on the currents. All the multiplied curves reasonably coincide with each other clearly indicating that the photoinduced electric currents are related to the second-order nonlinear optical response.

### B. Analytical consideration by perturbation theory

We will try to understand the numerical results of the photoinduced electric currents in an analytical way by perturbation theory. Although we solved the TDKS equation in our numerical analysis, we here proceed in a general many-body framework assuming that the TDDFT calculation provides an approximate description of fully correlated many-electron dynamics.

Instead of the pulse electric field, Eq. (5), employed in the numerical calculation, we take the following form convenient for the analytical treatment:

$$v_{\text{laser}} = exEe^{-\eta|t|}\cos\omega t \pm eyEe^{-\eta|t|}\sin\omega t, \tag{8}$$

where $\eta$ is a parameter of the pulse width. In the following we consider only the right-handed circularly polarized laser field without loss of generality. This field is expressed in the Fourier integral form of

$$v_{\text{laser}} = \frac{E}{2\pi}\int_{-\infty}^{\infty} d\omega' e^{-i\omega' t}\left\{(x-iy)\frac{\eta}{(\omega'+\omega)^2+\eta^2} + (x+iy)\frac{\eta}{(\omega'-\omega)^2+\eta^2}\right\}. \tag{9}$$

If the applied laser frequency $\omega$ is close to the excitation energy, only the second term contributes in the resonant excitation. We denote the energy and the wave function of the ground state in the absence of the laser pulse as $\omega_g$ and $|u_g\rangle$. The excited states associated with the electric current are considered to be doubly degenerate and their energies and wave functions are denoted as $\omega_\alpha$ and $|u_\alpha^{(\pm)}\rangle$, respectively. The signs of ± correspond to the right- and left-handed electric currents. For the planar molecules with $C_n$ symmetry considered in this study, the following selection rules are assumed to be satisfied:

$$\langle u_\alpha^{(\pm)}|x \pm iy|u_g\rangle \neq 0, \tag{10a}$$

$$\langle u_\alpha^{(\pm)}|x \mp iy|u_g\rangle = 0. \tag{10b}$$

Taking account of these selection rules under the resonance condition where the applied laser frequency $\omega$ is close to the excitation energy, $\hbar\omega_{\alpha g} = \hbar(\omega_\alpha - \omega_g)$, we obtain the following photoexcited wave function in the first-order perturbation theory:

$$|\psi(t)\rangle = |u_g\rangle e^{-i\omega_g t} + c^{(+)}|u_\alpha^{(+)}\rangle e^{-i\omega_\alpha t}, \tag{11}$$

where the coefficient $c^{(+)}$ after the applied pulse field ends is given by

$$c^{(+)} = \frac{E}{i}\frac{\eta}{(\omega_{\alpha g}-\omega)^2+\eta^2}\langle u_\alpha^{(+)}|x+iy|u_g\rangle. \tag{12}$$

We next give an expression of the electric current circulating in the molecule in the excited states, $u_\alpha^{(\pm)}$. When the particles of mass $m$ and charge $e$ circulate along a ring of radius $R$, there holds a relation between the total angular momentum $L(=L_z)$ and the electric current $eJ$ as follows:

$$L_z = 2\pi m R^2 J. \tag{13}$$

Employing this relation we define the current in a ring-shaped molecule when the molecule is in the excited state $u_\alpha^{(+)}$ by

$$J_\alpha^{(+)} = \frac{\langle u_\alpha^{(+)}|\hat{L}_z|u_\alpha^{(+)}\rangle}{2\pi m R^2}, \tag{14}$$

where $\hat{L}_z$ is the angular momentum operator. The photoexcited wave function is given by Eq. (11) after the laser pulse is switched off. However, the matrix element $\langle u_\alpha^{(+)}|\hat{L}_z|u_g\rangle$ vanishes for molecules with inversion symmetry because we assume that the excited state $u_\alpha^{(+)}$ is dipole active. Therefore, we have the following expression for the electric current:

$$eJ = e|c^{(+)}|^2 J_\alpha^{(+)} = e\frac{E^2}{2\pi m R^2\eta^2}|\langle u_\alpha^{(+)}|x+iy|u_g\rangle|^2\langle u_\alpha^{(+)}|\hat{L}_z|u_\alpha^{(+)}\rangle. \tag{15}$$

When deriving this equation, we utilized the resonance condition of $\omega = \omega_{\alpha g}$. This relation of Eq. (15) is second order in the strength of the electric field $E$, and thus is consistent with the observation in our numerical calculation that the electric current is ascribed to the second-order nonlinear optical response.

Here we note that the second-order term in the wave function should also be included in Eq. (11) to calculate the quantities associated with the second-order nonlinear optical response. In our present analysis, however, the second-order term in the wave function is not important because the first-order amplitude of the resonantly excited state is very large. Thus, the diagonal matrix element of the first-order wave function, Eq. (14), makes a dominant contribution to the second-order quantity.

Let us finally estimate the electric current by using Eq. (15). We need to evaluate the matrix elements, $\langle u_\alpha^{(+)}|x+iy|u_g\rangle$ and $\langle u_\alpha^{(+)}|\hat{L}_z|u_\alpha^{(+)}\rangle$. The former matrix element can be rewritten by the oscillator strength obtained in the linear response TDDFT calculations:

$$f_{\alpha g} = \frac{2m\omega_{\alpha g}}{3\hbar}2|\langle u_\alpha^{(+)}|x+iy|u_g\rangle|^2, \tag{16}$$

where the factor of 2 means that the oscillator strength is shared by the two states, $u_\alpha^{(\pm)}$. For the latter matrix element, we can simply take

$$\langle u_\alpha^{(+)}|\hat{L}_z|u_\alpha^{(+)}\rangle = \hbar\,. \tag{17}$$

This is an exact expression for a completely circular ring where $\hat{L}_z$ commutes with the Hamiltonian and the excited states are the eigenstates of $\hat{L}_z$. To calculate the electric current, we take a set of parameters of Eq. (15) for benzene; $R = 1.4$ Å, $1/\eta = 2$ fs, $T = 6$ fs, and $f = 1.0$ for the absorption peak at 6.89 eV. Substituting these values into Eq. (15), we obtain the electric current, $eJ = 8.7$ nA. This is qualitatively in good agreement with the calculated value of 7.0 nA.

It should be stressed that the clear second-order nonlinear effect was recognized in the laser intensity regime considered here. As the laser intensity becomes stronger, more complicated nonlinear effects would appear. We preliminarily confirmed that such nonlinear effects suppressed the photoinduced electric currents.

### C. Magnetization in ring-shaped molecules

The photoinduced electric currents circulating in the ring-shaped molecules inevitably give rise to the magnetic moments, so that the nonmagnetic molecules of $\text{Na}_{10}$ and benzene are considered to be magnetized. Such photoinduced magnetization is conceptually related to that in the work by Pershan and co-workers [27]. They demonstrated that the magnetization was induced by a magneto-optical response associated with an inverse phenomenon of the Faraday effect, and thus referred to this effect as the inverse Faraday effect (IFE). Very recently, Kimel *et al.* coherently controlled spin oscillations in the weak ferromagnet $\mathrm{DyFeO_3}$ by using IFE [28]. The Faraday effect is well known as a phenomenon that the polarization plane of linearly polarized light is rotated when the light propagates through magnetic compounds. The Faraday rotation $\alpha$ is proportional to the magnetization $M$ and given by

$$\alpha = \frac{\chi}{n} Mk, \tag{18}$$

where $\chi$ is the magneto-optical susceptibility, $n$ is the refractive index, and $k$ is the wave vector of the light.

The photoinduced electric currents and magnetic moments considered in the present study may be detectable through the Faraday effect by means of a pump-probe experiment as follows. The pump pulse (i.e., the circularly polarized laser pulse) induces the electric currents in the ring-shaped molecule and the magnetic moments are simultaneously induced. Then, if the probe pulse (i.e., the linearly polarized laser pulse) is applied to the molecule, we can detect the rotation of the polarization plane of the probe pulse. The rotation of the polarization plane is proportional to the photoinduced magnetization as given by Eq. (18) [29]. If the probe pulse is applied with a delay after the end of the pump pulse and the Faraday rotation is measured as a function of the delay time, we can also observe the relaxation (or dissipation) of the electric currents caused by electron-phonon couplings or interaction with environment. Although we cannot simulate such a pump-probe experiment within the present theory, the electronic relaxation processes related to the electronic decoherence are very important in elucidating the electron dynamics in molecular systems with dissipation. We are currently studying the electron dynamics interacting with an electron reservoir.

## IV. CONCLUDING REMARKS

We have theoretically simulated the photoinduced electric currents in the ring-shaped molecules $\mathrm{Na_{10}}$ and benzene by the circularly polarized laser pulses. The electron dynamics of the currents was described by performing the TDDFT calculations in real space. The following three features have been revealed. First, the electric currents were strongly dependent on the applied laser frequency and induced much more effectively under the dipole resonance condition. The on-resonance photoinduced electric currents persisted continuously even after the end of the laser pulse, i.e., without the electric field. Second, the photoinduced electric currents were found to be attributed to the second-order nonlinear optical response. This nonlinear effect was analytically explained by using perturbation theory. Third, the circularly polarized laser pulses induced the ring currents much more effectively than the method using static magnetic fields. The ring currents inevitably induce the magnetic moments. For these reasons, the means of the photoinduced electric currents and magnetic moments by the circularly polarized laser pulses has a potentiality for its application to development of molecular-sized quantum devices functioning as magnetic memory storages.

## ACKNOWLEDGMENTS

The present work was supported by Grant-in-Aid (No. 17550024, No. 18066019, No. 18036002, No. 18540366) and by the Next Generation Super Computing Project, Nanoscience Program, from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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[29] In reality, it is not easy to measure the magnetization through such an experimental design. Taking account of the fact that the magnetic moment considered here is proportional to the square of the radius, it might be possible to carry out the experiment by preparing a ring-shaped molecule with a sufficiently large radius, a semiconductor nanoring (and also an array of the nanorings), or a ring-shaped molecule in the condensed phase (e.g., solid benzene).