Resolving Multiple Molecular Orbitals Using Two-Dimensional High-Harmonic Spectroscopy

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High-harmonic radiation emitted from molecules in a strong laser field contains information on molecular structure and dynamics. When multiple molecular orbitals participate in high-harmonic generation, resolving the contribution of each orbital is crucial for understanding molecular dynamics and for extending high-harmonic spectroscopy to more complicated molecules. We show that two-dimensional high-harmonic spectroscopy can resolve high-harmonic radiation emitted from the two highest-occupied molecular orbitals, HOMO and HOMO-1, of aligned molecules. By the application of an orthogonally polarized two-color laser field that consists of the fundamental and its second-harmonic fields to aligned CO_2 molecules, the characteristics attributed to the two orbitals are found to be separately imprinted in odd and even harmonics. Two-dimensional high-harmonic spectroscopy may open a new route to investigate ultrafast molecular dynamics during chemical processes.

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High-harmonic radiation generated from aligned molecules can be parsed to reveal the structures or dynamics of molecular orbitals [1–4]. In the process of high-harmonic generation (HHG), an electron is ionized and accelerated by an intense laser field and then recombines with the parent ion [5]. Coherent interference between the returning electron and the molecular orbitals induces an oscillating dipole, leading to HHG [6]. Since the oscillating dipole is sensitive to the orbital structure, the characteristics of the molecular orbital can be revealed by HHG. The ionization, the first step of HHG, is a highly nonlinear process that is very sensitive to the laser intensity and ionization potential. When multiple molecular orbitals are exposed to a strong laser field, the highest-occupied molecular orbital (HOMO) is mostly ionized and thus emits strong high-harmonic radiation. The radiation from the energetically lower-lying molecular orbital (HOMO-1) is often too weak to distinguish from the dominant contribution of the HOMO. This naturally leads to difficulty in investigating the dynamics of the HOMO-1.

In some special cases, it is possible to observe the radiation from the HOMO-1. With N_2, for example, the HOMO with σ_g symmetry and the HOMO-1 with π_u symmetry can have strong induced dipole moments parallel and perpendicular to the molecular axis, respectively. This makes it possible to distinguish harmonic signals from the HOMO and HOMO-1 by varying the alignment angle and has been used to demonstrate the contribution of multiple orbitals to HHG [7] and to reconstruct the HOMO and the HOMO-1 using a tomographic method [8]. In the case of molecules such as O_2 and CO_2 with the π_g symmetry of HOMO, these approaches cannot be applied because the HOMO does not exhibit such orbital symmetry of N_2. As a consequence, a new approach is required to explicitly resolve the characteristics of multiple molecular orbitals.

In this Letter, we demonstrate a novel method to observe the characteristics of HOMO and HOMO-1 of molecules using two-dimensional high-harmonic spectroscopy (HHS). In our HHS, an orthogonally polarized two-color laser field, consisting of the fundamental (1ω) and its second harmonic (2ω), is applied to aligned molecules in order to reveal the characteristics of multiple molecular orbitals. HHS using two-color laser fields has previously been used to probe the symmetry of the HOMO using selective ionization parallel to laser polarization [9,10] or to detect the ionization times of HOMO and HOMO-2 of the CO_2 molecule [11]. The previous approaches cannot resolve the contributions of the HOMO and HOMO-1 for such molecules having strong dipole moments in orthogonal directions due to the absence of molecular alignment [9,10] or a weak perturbative second-harmonic field [11]. In our HHS, the characteristics of multiple molecular orbitals are separately embedded in odd and even harmonics—two separate channels to resolve HOMO and HOMO-1.

To be more specific, it is helpful to consider the recombination process of molecules in an orthogonally polarized two-color laser field. The two-color laser field can be described by $\vec{E}(t) = \hat{x}E_1\cos(\omega t) + \hat{y}E_2\cos(2\omega t + \phi)$, where E_1 and E_2 are the amplitudes of the fundamental and second-harmonic (SH) fields, respectively. Here, ω is the

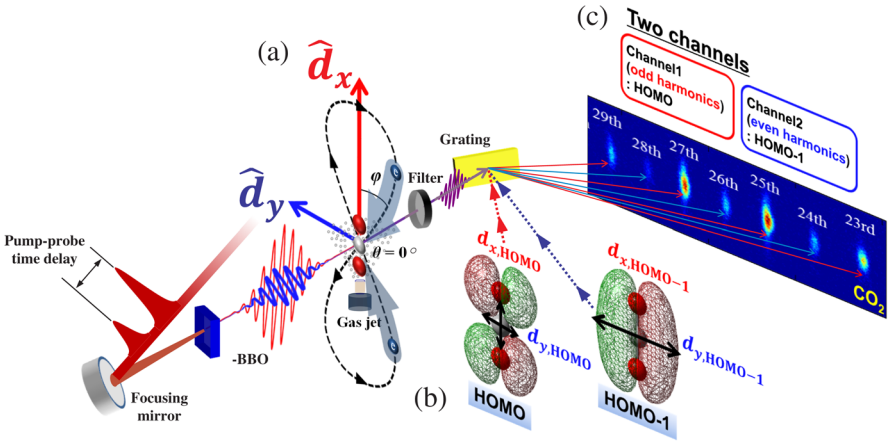

FIG. 1 (color online). Schematic layout for two-dimensional high-harmonic spectroscopy for probing multiple molecular orbitals. (a) Recombination in an orthogonally polarized two-color laser field. Temporal variation of the two-color laser field is depicted as a black dashed line. Emitted odd and even harmonics are polarized to $\hat{d}_x$ and $\hat{d}_y$, respectively. (b) Orbital structures and induced dipole moment of the HOMO and HOMO-1 in CO_2. The length of the arrow indicates the relative strength of the oscillating dipole moment due to the structure. (c) The spectral image shows a typical harmonic spectrum from aligned CO_2 molecules. The HOMO and HOMO-1 can be separately encoded in the odd and even harmonics by the different strength of dipole moment induced in the two-color laser field on the two orthogonal axes.

fundamental laser frequency, and ϕ is the relative phase of the SH field to the fundamental field [12]. The black dashed lines with arrows in Fig. 1(a) represent the temporal variation of the two-color electric field. In this configuration, the returning electron is incident to the parent ion at an angle ϕ in each half optical cycle because the recombination process is dominated by the ionized electron only in the straight portion of the electric field of the two-color laser field [13].

During the recombination, multiple orbitals produce different oscillating dipoles on the two orthogonal axes. The HOMO and HOMO-1 in CO_2 have antibonding π_g symmetry and bonding π_u symmetry, respectively, as shown in Fig. 1(b). If we consider only the HOMO and HOMO-1 in the HHG process, the induced dipole moment d can be expressed as $d_{\mathrm{HOMO}} + d_{\mathrm{HOMO-1}}$. This can be decomposed into $d_x(= d_{x,\mathrm{HOMO}} + d_{x,\mathrm{HOMO-1}})$ and $d_y(= d_{y,\mathrm{HOMO}} + d_{y,\mathrm{HOMO-1}})$, where the x axis lies in the polarization direction of the fundamental laser field as shown in Fig. 1. For the HOMO-1, the dipole moment along the x axis ($d_{x,\mathrm{HOMO-1}}$) is cancelled out because two dipole moments, induced with the x axis as the center, are out of phase, owing to the antisymmetry of the HOMO-1 on the x axis. On the other hand, the symmetric HOMO-1 in the y axis induces a relatively large dipole moment ($d_{y,\mathrm{HOMO-1}}$). The HOMO is antisymmetric on both axes, but small dipole moments can be induced when the returning electron passes through the center of the HOMO [14]. Thus, d_x is dominated by $d_{x,\mathrm{HOMO}}$ because of the negligible contribution from HOMO-1, and d_y is mainly attributable to the HOMO-1 because of the larger $d_{y,\mathrm{HOMO-1}}$. Since d_x and d_y correspond to odd and even harmonics in the two-color scheme, the characteristics of the HOMO and HOMO-1 would be projected to odd and even harmonics, respectively.

In order to prove that our strategy is feasible, we performed first-principles calculations based on time-dependent density functional theory (TDDFT). We calculated harmonic spectra from the Fourier transform of time-dependent dipole acceleration using a real-time and real-space TDDFT code [15]. The effect of core electrons was taken into account by norm-conserving pseudopotentials with a separable approximation [16,17]. To calculate the exchange-correlation potential in TDDFT, an adiabatic local density approximation was used [18]. For the laser intensities of 9.2×10^{13} and 1.1×10^{13} W/cm^2 at ω and 2ω, respectively, we obtained high-harmonic spectra with aligned and antialigned CO_2 molecules including multiorbital contributions.

The preceding qualitative discussion implies that, when CO_2 is aligned with the fundamental laser polarization, intensity for even harmonics could increase due to the relatively large dipole moment of the HOMO-1. Figure 2(a) shows the harmonic spectra calculated for all valence orbitals in CO_2 exposed to an orthogonally polarized two-color laser field. For harmonics above the 27th order [indicated by arrows and represented with symbols in Fig. 2(d)], even harmonics increase when CO_2 is aligned, i.e., the angle between the fundamental laser polarization and the molecular axis, $\theta = 0°$. In order to confirm that the increase comes from the HOMO-1, we performed calculations with a single orbital. In Fig. 2(b), both odd and even harmonics of the HOMO decrease when CO_2 is aligned. This reduction can be attributed to structural interference [2,19]. Conversely, the even harmonics in Fig. 2(c), calculated from the HOMO-1, increase as expected. The opposite response of the HOMO and HOMO-1 indicates that the increase in the even harmonics, calculated with all

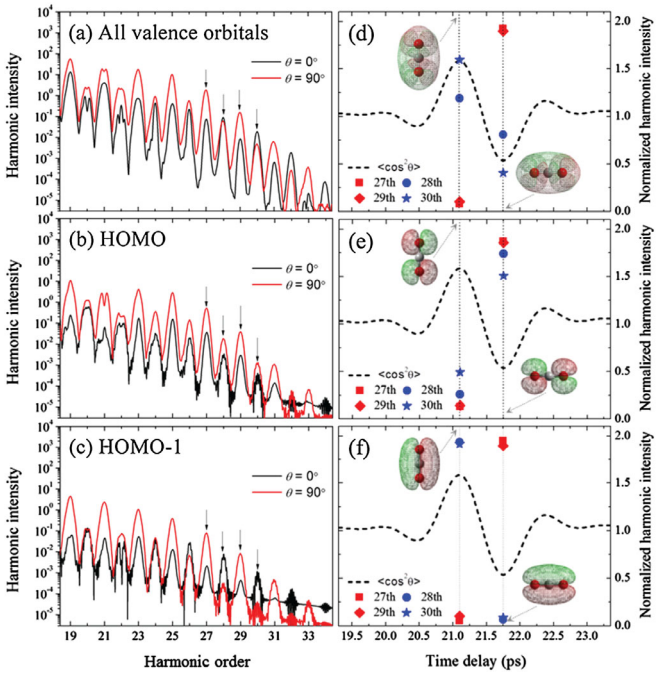

FIG. 2 (color online). Calculated harmonic spectra with the three different orbital configurations for (a) all valence orbitals, (b) HOMO, and (c) HOMO-1. The black and red lines correspond to alignment and antialignment, respectively. [(d)–(f)] The calculated harmonic intensities from the 27th to 30th harmonics, indicated with arrows in (a)–(c). The dashed line shows the degree of alignment. Calculated intensities are normalized against the randomly aligned case.

valance orbitals, is caused by the HOMO-1. The HOMO and HOMO-1 are responsible for the decrease in odd harmonics and increase in even harmonics, respectively. Thus, the calculations confirm that the multiple orbitals can be separately characterized by observing odd and even harmonics generated in the two-color laser field.

For the experimental demonstration of two-dimensional HHS, we generated high harmonics from aligned molecules using an orthogonally polarized two-color field. The experiments were performed using a femtosecond Ti: sapphire laser operating at 1 kHz. The schematic layout of the experimental setup is shown in Fig. 1. Laser pulses with duration of 28 fs at 790 nm were divided into two parts by an 8:2 beam splitter, and the two pulses were recombined with time delay. The positive time delay means that the pump pulse precedes the probe pulse. The weak pump pulse was used for molecular alignment, and the strong probe pulse for HHG. For the SH generation, a 100-μm thick beta-barium borate (BBO) crystal (type I), placed 20 cm from the gas jet, was used. The SH was, then, orthogonally polarized with respect to the fundamental field. The laser intensities were 5.3×10^{13} W/cm^2(1ω) and 3.1×10^{12} W/cm^2(2ω) for the pump and 3.6×10^{14} W/cm^2(1ω) and 4.5×10^{13} W/cm^2(2ω) for the probe. Although the pump pulse contains SH in this configuration, the SH of the pump pulse was too weak to affect the impulsive molecular alignment. The relative phase between the fundamental and the SH field was measured by observing HHG with phase modulation [13]. We set the relative phase to 0.5π for maximizing the even harmonic yield. Two pulses were focused to a gas jet with a nozzle diameter of 0.5 mm using a spherical mirror with an f number of 45. The jet was positioned about 6 mm in front of the focal plane for an optimal phase matching [20]. The high harmonics were detected using a flat-field extreme ultraviolet spectrometer.

The high-order harmonics from N_2 and CO_2 molecules, measured with respect to the time delay between the aligning laser pulse (pump) and the fundamental laser pulse (probe), are shown in Fig. 3. The time delay is set to approximately $T_{\rm rot}/2$ ($T_{\rm rot}$: rotational period), where the degree of alignment ($\langle\cos^2\theta\rangle$) switched rapidly from aligned ($\langle\cos^2\theta\rangle \approx 1$) to antialigned ($\langle\cos^2\theta\rangle \approx 0$). Additionally, the temporal evolution of the degree of alignment calculated with an initial rotational temperature of 90 K is represented by the dashed black line for comparison. Figure 3(a) shows harmonic intensities obtained from N_2. In the case of N_2, the structural interference, occurring in the HOMO of CO_2, does not take place. Odd harmonics from the HOMO, thus, do not show an inverted behavior to the degree of alignment; both odd and even harmonic intensities show the same behavior as the evolution of the degree of alignment. Figure 3(b) shows the harmonic intensities obtained from CO_2. The intensity of odd harmonics (25th and 27th harmonics) from CO_2 is inversely proportional to the degree of alignment, whereas the evolution of even harmonics (24th and 26th harmonics) follows the degree of alignment. These observed features coincide with the calculated results in Fig. 2(d). In addition, Fig. 3(c) shows normalized harmonic intensities generated from aligned CO_2, which clearly reveals the separation between odd and even harmonics for nine orders. These measurements confirm that the two-dimensional HHS resolves multiorbital characteristics encoded in the different harmonic orders.

The harmonic spectrum in Fig. 4(a), obtained in the orthogonally polarized two-color laser field, shows the characteristic features of the HOMO and HOMO-1. The odd harmonics in the plateau region are much stronger than the even harmonics, while the even harmonic in the cutoff has slightly higher intensity than the odd cutoff harmonic. The inversion between odd and even harmonic intensities in the plateau and in the cutoff reflects the higher ionization potential of HOMO-1 than that of HOMO [3,7]. In addition, a dip structure due to the dynamical destructive interference between HOMO and HOMO-2 was not observed in the odd harmonic spectrum. The dynamical destructive interference was observed in the single-color harmonic spectrum shown in Fig. 4(b), as consistent with previous studies [3,21,22]. In the two-color scheme,

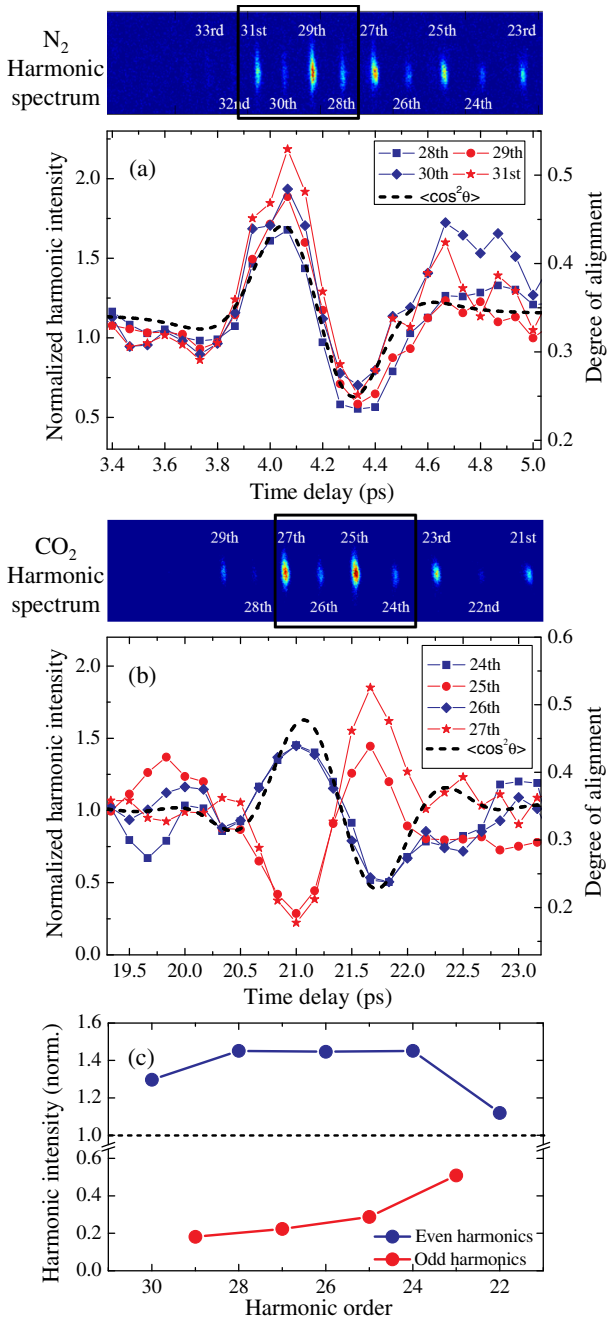

FIG. 3 (color online). Harmonic spectra generated by an orthogonally polarized two-color laser field and the change of harmonic intensities with respect to pump-probe time delay: (a) N_2, (b) CO_2. The time domain is set to $T_{rot}/2$ (T_{rot}: rotational period, 8.4 ps for N_2, 42.5 ps for CO_2). Right axis: degree of alignment, $\cos^2\theta$ (calculation, dashed black line). Left axis: normalized harmonic intensity (experiment, line plus symbol). (c) Normalized odd (red) and even (blue) harmonic intensities generated from aligned CO_2 molecules. Harmonic intensities are normalized against the randomly aligned case.

however, the direction of dominant ionization for HHG is tilted by about 30° from the fundamental polarization, as described in Fig. 1(a). The ionization probability of the HOMO is greatly enhanced at this angle as compared to the

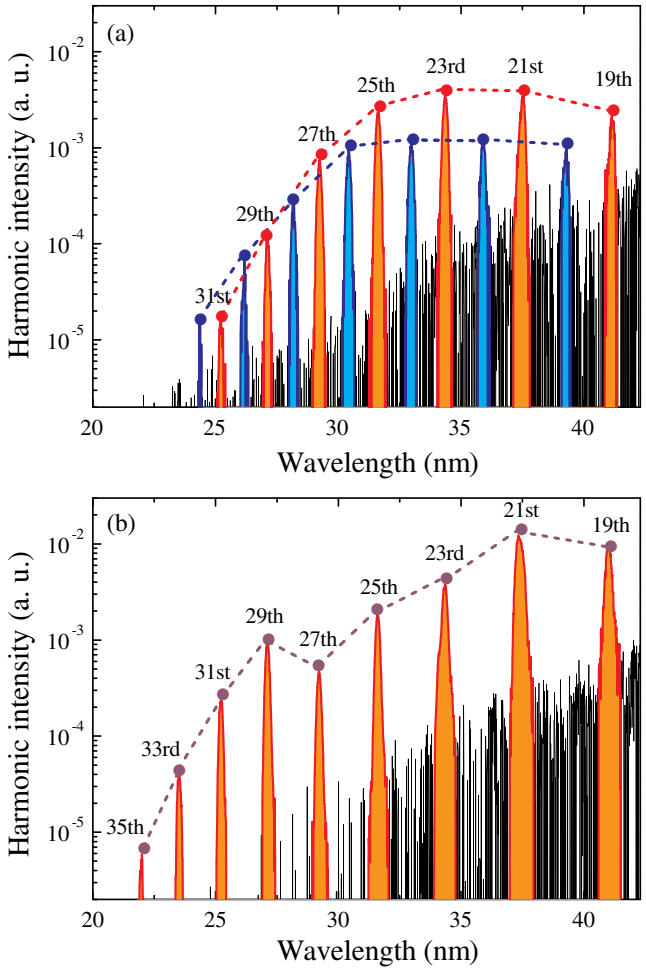

FIG. 4 (color online). Harmonic spectra generated from aligned CO_2 molecules (a) in the orthogonally polarized two-color laser field and (b) in a single-color laser field.

case of $\varphi = 0°$, while that of HOMO-2 is slightly reduced [23]. The odd harmonics were, thus, dominantly generated from the HOMO due to the much larger ionization probability of HOMO than that of HOMO-2 in the orthogonally polarized two-color laser field. Consequently, the contribution of the HOMO-2 to our experimental results was not significant, and the characteristics of HOMO and HOMO-1 could be independently revealed through odd and even harmonics.

In conclusion, we demonstrated a new method for resolving multiple molecular orbitals. Our theoretical and experimental results show that high-harmonic spectroscopy can be extended from one to two dimensions in the laboratory frame by employing an orthogonally polarized two-color laser field with aligned molecules. In the two-dimensional HHS, the structural characteristics of multiple orbitals, HOMO and HOMO-1, are separately imprinted in odd and even harmonics. Our approach would be applicable to a variety of molecules, such as O_2, Cl_2, Br_2, I_2 and CO, if a strong dipole moment is induced along orthogonal directions in the two-color laser field. In addition, when

it is combined with other interferometric approaches [3], the technique would also be generally applicable for simple molecules. This should lead to independent and simultaneous observation of the structures and dynamics of multiple orbitals and enable the observation of multiorbital dynamics during chemical reactions of more complicated molecules.

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