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 CO2 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, an electron is ionized and accelerated by the 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 N2, for example, the HOMO with \( \sigma_g \) symmetry and the HOMO-1 with \( \pi_u \) 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 O2 and CO2 with the \( \pi_u \) symmetry of HOMO, these approaches cannot be applied because the HOMO does not exhibit such orbital symmetry of N2. 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 (\( \omega \)) and its second harmonic (\( 2\omega \)), 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 CO2 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 \( \hat{E}(t) = \hat{E}_1 \cos(\omega t) + \hat{E}_2 \cos(2\omega t + \phi) \), where \( E_1 \) and \( E_2 \) are the amplitudes of the fundamental and second-harmonic (SH) fields, respectively. Here, \( \omega \) is the...
fundamental laser frequency, and $\phi$ 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 $\phi$ 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 $\pi_d$ symmetry and bonding $\pi_u$ 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 $d_{\text{HOMO}} + d_{\text{HOMO}-1}$. This can be decomposed into $d_x = d_{x,\text{HOMO}} + d_{x,\text{HOMO}-1}$ and $d_y = d_{y,\text{HOMO}} + d_{y,\text{HOMO}-1}$, 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 ($d_{x,\text{HOMO}-1}$) 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 ($d_{y,\text{HOMO}}$). 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 $d_{x,\text{HOMO}}$ because of the negligible contribution from HOMO-1, and $d_y$ is mainly attributable to the HOMO-1 because of the larger $d_{y,\text{HOMO}-1}$. 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 $9.2 \times 10^{13}$ and $1.1 \times 10^{13}$ W/cm$^2$ at $\omega$ and $2\omega$, 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, $\theta = 0^\circ$. 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
Although the pump pulse contains SH in this orthogonally polarized with respect to the fundamental, 20 cm from the gas jet, was used. The SH was, then, combined 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 pulse was used for molecular alignment, and the strong fundamental laser pulse generates 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 $T_{\text{rot}}/2$ ($T_{\text{rot}}$: rotational period), where the degree of alignment ($\cos^2\theta$) switched rapidly from aligned ($\cos^2\theta \approx 1$) to antialigned ($\cos^2\theta \approx 0$). 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].
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 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 \( \text{O}_2 \), \( \text{Cl}_2 \), \( \text{Br}_2 \), \( \text{I}_2 \) and \( \text{CO} \), 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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