Observing molecular structures by using high-order harmonic generation in mixed gases

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We demonstrate that the structure of CO_2 molecules can be determined by measuring the phases of harmonics from them. This is evidenced by observing a phase jump of harmonics generated in a mixed gas of aligned CO_2 molecules and their reference Kr atoms, which serve to extract the net contribution due to the structure of CO_2 molecules. Furthermore, in the strong field approximation model, we derive the exact conditions of quantum interference during high-order harmonic generation in CO_2 molecules analytically and we propose a method to control harmonic pulse duration.

High-order harmonic generation (HHG) in atoms and molecules is widely accepted as a robust method to obtain coherent ultrashort radiation in the extreme ultraviolet and soft x-ray regions [1–4]. The ultrafast generation mechanism of harmonics [5,6] simultaneously offers us novel methods to observe the structures of molecules. One approach is simply to measure the harmonic intensities (I_{HH}) from the molecules and all of the attempts were performed based on this method [7–11]. Since stationary conditions of harmonic phases determine the dynamics to be realized, the phases should contain the crucial information on the molecular structures. Lack of simple methods to measure them, however, prevented researchers from obtaining this remaining grail.

Recently, the present authors introduced precisely controlled mixed gases as nonlinear media for HHG [12–15] and demonstrated a novel method to measure harmonic phases [12,15]. The method is based on the interference of harmonics generated in each gas, which naturally takes place during HHG in mixed gases, and the observed phase was found to encode the underlying electron dynamics in the atoms and molecules [12]. According to the standard model of HHG, the electron dynamics are composed of three quantum transitions [5,6]: (i) ionization, (ii) acceleration in the laser field, and (iii) recombination back into the bound electronic state. In the case of atoms with simple potentials, the electron dynamics are mainly determined by their ionization potentials I_p, while in the case of molecules the structures of them give additional effects. Accordingly, if we measure the harmonic phases from a pair of atoms and/or molecules with (almost) the same I_p, the net effects due to the structures of the molecules are expected to be extracted.

In fact, as depicted in Fig. 1, the harmonic phase is predicted to jump by $\sim \pi$ in a typical experimental condition [16]. Due to the accidental fact that de Broglie wavelength of recombining electron in the third step is comparable to the molecular size, geometrical relation between the recombining electron and its "doppelganger" remaining in the molecule can interfere destructively [8] (destructive interference; DI) and correspondingly the phase can jump around the DI [16]. Therefore, observation of the phase jump corresponds to that of the geometry of Fig. 1(c) and is expected to determine the molecular structure by regarding the electron wave-

length as a gauge. In principle, such a molecular imaging is also possible by measuring I_{HH} as a function of some parameters such as orientation angle θ [7]. I_{HH} is, however, a high-order complex function in general and correspondingly it is often assumed that molecules are perfectly aligned so that all of them respond in phase [7]. Such assumptions, however, are a somewhat rough approximation [8–10]. Because of the uncertainty relation of quantum mechanics and geometrical reasons described in the following, one cannot obtain any signals from perfectly aligned molecules. Furthermore, ionization of the molecules by the alignment pulse strongly limits the available maximum intensity of the pulse. One powerful solution is to focus on some integrated signals from the molecular ensemble with angular distribution *ab origine*. In fact, the first clear observation of DI during HHG was demonstrated by observing the anticorrelation between integrated harmonic intensities and ion yield [8]. Due to the simple behavior of harmonic phase (Fig. 1), the phase of integrated harmonics from the ensemble is expected to be a crucial index to determine molecular structures with no prerequisite. In fact, as pointed out in Ref. [17], the phase information must be implicitly assumed for the method based on intensity measurement [7] to determine the complex dipole moment from the measured $I_{HH}(\theta)$.

In this Rapid Communication, we demonstrate that the structure of CO_2 molecules can be determined by measuring the phases of harmonics from them. This is evidenced by
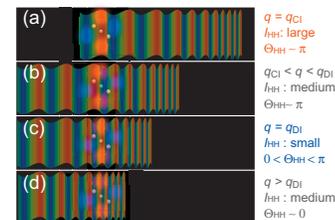

FIG. 1. (Color) Schematic diagrams illustrating the recombination process of HHG in a CO_2 molecule. Harmonic phases Θ_{HH} as well as intensities I_{HH} change according to the relation between HOMO and the de Broglie wave of the recombining electron. When the phase of the electron wave correlates or anticorrelates with that of HOMO, CI (a) or DI (c) take place, respectively. The phases of harmonics change dramatically at DI. When the short trajectory is selected by a focusing geometry, the recombining electron wave packet is positively chirped and its wavelength corresponds to the harmonic order q and excursion time τ of electron one to one.
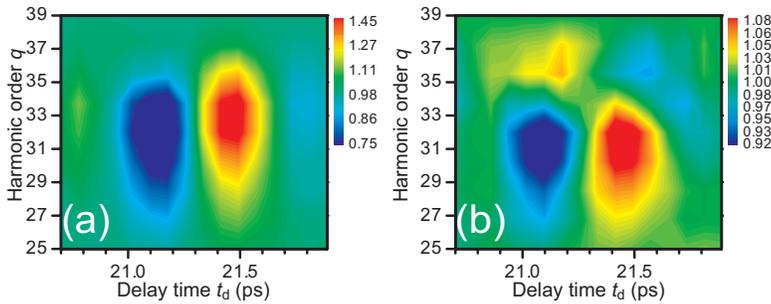
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FIG. 2. (Color) The harmonic spectra from a CO_2 gas (a) and a mixed gas of CO_2 and Kr (b) as functions of time delay t_d at around the half rotational revival of CO_2. At the 35th and 37th harmonics, the signal from the CO_2 gas and the CO_2-Kr gas anticorrelate to each other. The rotational period of a CO_2 molecule is 42.7 ps.

observing a phase jump of harmonics [16] generated in a mixed gas of aligned CO_2 molecules and their reference Kr atoms, which serve to extract the net contribution due to the structure of CO_2 molecules. Furthermore, in the SFA model [6], we derive the exact conditions of quantum interference during HHG in CO_2 molecules analytically and propose a method to control harmonic pulse duration.

An output from a Ti:sapphire laser having a pulse width of ~40 fs and a center wavelength of ~800 nm is split into two pulses. The first pulse is used as a pump to create rotational wave packets and induce nonadiabatic molecular alignment [7–10,18]. The second pulse is delayed by a computer controlled translation stage and is used as a probe to generate high harmonics. The two pulses were loosely focused with a lens ($f=2.4$ m) into an interaction gas cell ($L=1.5$ cm) filled with a pure and/or a mixed gas, with which we can control Kr and CO_2 gases with different hydrodynamic behavior under the same condition precisely (SEM of gas pressure ~0.2% [12]). Phase-matched harmonics were generated in the cell by balancing the Gouy phase and the negative dispersion of the gas medium [3]. The intensity of the pump pulse is ~6×10^{13} W/cm^2 and that of the probe is ~2×10^{14} W/cm^2, which is below the saturation intensity. The generated harmonics were spectrally resolved with a flat-field grating and detected by a microchannel plate and a CCD camera.

Figure 2 shows typical harmonic intensities from a CO_2 gas (2.67 Torr) and a mixed gas of CO_2 and Kr (4.00 Torr; the mixing ratio=2:1) as functions of the delay t_d between pump and probe pulses. The delay is set at around the half revival region of the molecular rotation ($t_d=21-22$ ps). The number densities of CO_2 molecules in the gases are set to be the same and the signals are normalized to those of the base lines. From 25th to 31st harmonics, the harmonic signals from the CO_2 gas and those from the CO_2-Kr gas correlate with each other. This observation is intuitively reasonable;

when the signals from one component are suppressed (enhanced), total signals should be suppressed (enhanced). These suppressions and enhancements are due to alignment and antialignment of molecular samples, respectively, and the anticorrelation between harmonic intensity and degree of alignment is related to DI during HHG [8]. For harmonics higher than 33rd, however, these two signals anticorrelate with each other. In particular, at $t_d \sim 21.2$ ps, the HHG in the CO_2-Kr gas is enhanced despite the suppression of HHG in its constituent CO_2 gas [19]. This counterintuitive observation can be explained only by considering that the relative phase between the two harmonics dramatically changes at the half revival so that the interference condition changes. In fact, when HHG in CO_2 is suppressed, CO_2 is aligned and thus the population of region I [Fig. 3(b)] is increased. As is discussed in the following, the harmonic phase in region I is $\Theta_{HH} \sim 0$, and the harmonics from CO_2 interferes with those from Kr constructively enough to enhance the total harmonic signals from the mixed gas.

Group theory gives us a clear understanding for the present physics. Figure 3(a) shows the symmetry of a single CO_2 molecule, whose axis C aligns at an angle θ to the electric fields **E** of pump and probe pulses. The symmetry of the CO_2 molecule is $D_{\infty h}$ (Ref. [8]) and from quantum chemical analysis, π_g is the symmetry of HOMO (the highest occupied molecular orbital), which is one of the irreducible representations of $D_{\infty h}$ and plays dominant roles in HHG. Although HOMO is doubly degenerated with angular momentum $L=\pm 1$ along C, one can always choose two real basis functions so that one orients parallel to the plane σ_v and the other perpendicular to σ_v. The latter orbital ["dark" HOMO in Fig. 3(a)] does not contribute to HHG due to its antisymmetry with respect to σ_v. The "relevant" HOMO has two mirror antisymmetries with respect to σ_h and the plane that is parallel to C and perpendicular to σ_v, which lead to DI of HHG when $\theta = 0, \pi/2$, respectively. Finally, there is an-
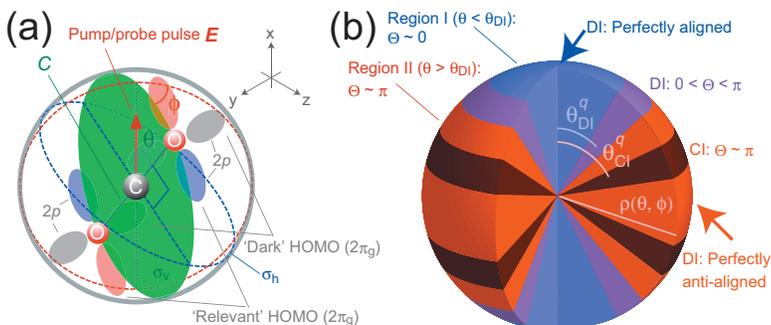

FIG. 3. (Color) The geometries of (a) a single CO_2 molecule and (b) a rotational ensemble of CO_2 molecules for the qth harmonic generation. Due to the principle of superposition, the generated harmonic fields in region I and those in region II interfere with each other destructively. Here x^{Kr} is chosen as a reference point of harmonic phases.

other kind of DI, which is related to the size of HOMO. The so-called two point emitter model [16] gives us the simplest picture of it, where the two $2p$ orbitals of the relevant HOMO play roles of the emitters. Intuitively, the first order DI ($\mu=0$) and CI (constructive interference, $\mu=1$) are expected to take place, when the phase of HOMO correlates and anticorrelates to that of the de Broglie wave

$$R \cos \theta'^q_{DI,CI} = (n - \delta^1_\mu/2)\lambda_q. \tag{1}$$

Here n is an integer (only $n=1$ is relevant in the present case), δ^ν_μ is the Kronecker delta, $\lambda_q = 2\pi/(2q\omega_0)^{1/2}$ is the de Broglie wavelength of the recombining electron for the qth harmonic generation, $R=0.232$ nm is the distance between the two O atoms in CO_2 (Ref. [8]).

An analytic consideration, however, indicates the above results for θ'^q_{DI} and θ'^q_{CI} should be modified by the finite and anisotropic structures of the $2p$ orbitals. For the qth harmonic generation, by using the steepest descent method, an induced dipole moment of the CO_2 molecule in Fig. 3(a) is given by [6]

$$\mathbf{x}_q(\theta) = 2\pi i/[\det(S)'']^{1/2}[2\pi/i\tau_s]^{3/2}e^{-iS+iqt_s}\mathbf{d}^*[\mathbf{p}'_s, \theta]$$
$$\times \mathbf{E}(t'_s) \cdot \mathbf{d}[\mathbf{p}_s - \mathbf{A}(t'_s), \theta]. \tag{2}$$

Here $\mathbf{p}_s = \int^{t_s}_{t'_s} dt'' \mathbf{A}(t'')/\tau_s$ with vector potential $\mathbf{A}(t'')$, $\mathbf{d}(p,\theta) := \langle \mathbf{p}|\mathbf{x}|\Psi_0\rangle$ is the bound-free dipole transition matrix element between the ground state $|\Psi_0\rangle$ and the continuum state $|\mathbf{p}\rangle$, $S^i = I_p\tau_s + [\tau_s - 2(1-\cos\tau_s)/\tau_s - C(\tau_s)\cos(2t_s-\tau_s)]U_p$ with the ponderomotive potential U_p and $C(\tau) := \sin\tau - 4\sin^2(\tau/2)/\tau$, and $\det(S)''$ is the determinant of the 2×2 matrix of the second derivatives of S with respect to t_s and t'_s. $I^{CO_2}_p = 13.78$ eV and $I^{Kr}_p = 14.00$ eV. Here, we set the parameter of electron acceleration [9] $\xi=0$, following the numerical model by Lein *et al.* (Ref. [16]); $\mathbf{p}'_s = \sqrt{2q}[\mathbf{p}_s - \mathbf{A}(t_s)]/|\mathbf{p}_s - \mathbf{A}(t_s)|$. The transition dipole moment for CO_2 is given by [9]

$$\mathbf{d}_{2\pi_g}(p,\theta) = N'[2i\sin(\mathbf{p}'_s \cdot \mathbf{R}/2)\mathbf{d}_{2p}(\mathbf{p}'_s, \pi/2-\theta)$$
$$- \cos(\mathbf{p}'_s \cdot \mathbf{R}/2)\phi_{2p}(\mathbf{p}'_s, \pi/2-\theta)\mathbf{R}], \tag{3}$$

where $\mathbf{d}_{2p}(\mathbf{p}'_s, \pi/2-\theta)$ and $\phi_{2p}(\mathbf{p}'_s, \pi/2-\theta)$ are the atomic dipole moment and the wave function of the $2p$ orbital of the O atoms, respectively. We adopt Slater-type orbitals (STO) rather [8,9] than Gaussian-type orbitals (GTO), since STO have the correct behavior as $|x| \to \infty$. The above picture of two point emitters is represented by the first term in Eq. (3) [9]. In fact, this term $[\sin(\mathbf{p}'_s \cdot \mathbf{R}/2)]$ is zero (maximized) when the condition of DI (CI) in Eq. (1) is satisfied. The second term, which is oriented along C, corrects the errors of the simple model. One should note that this correction term induces the same effect as when one increases I_p (Ref. [10]) and/or assumes perfectly aligned molecules [7]. The interesting thing is that the "exact" conditions for DI and CI can be derived analytically as

$$R \cos\theta^q_{DI,CI} = [(n - \delta^1_\mu/2) - \Phi(\theta^q_{DI})/\pi]\lambda_q, \tag{4}$$

and correspondingly, whole $\mathbf{d}_{2\pi_g}(p,\theta)$ [not the first term in Eq. (3) only] must change its phase by π at $\theta=\theta_{DI}$ as follows:

$$\Theta_{HH} \sim 0(\theta < \theta^q_{DI}) \quad \text{and} \quad \Theta_{HH} \sim \pi(\theta > \theta^q_{DI}). \tag{5}$$

Here, $\Phi(\theta) = \arctan\{[(2\pi/\lambda_q)^2 + (\zeta/2)^2](2\pi/\lambda_q)R\sin\theta \times\cos\theta]/\{2[(\zeta/2)^2 - 5(2\pi/\lambda_q)^2\sin\theta]\}\}$ with $\zeta\sim2.25$ being the scale factor of the $2p$ orbitals. Notice that phase jump around DI is one of the universal characteristics of interference phenomena in physics.

Experimentally observed signals, even from "aligned" molecules, are coherent superpositions of harmonic fields generated in molecules with anglar distribution, whose roles can be included by considering the axial symmetry of a rotational wave packet [Fig. 3(b)]. The probability density $\rho(\theta,\phi)$ should be independent of ϕ and one can write the population in $[\theta, \theta+d\theta]$ as $\rho(\theta)d\theta = 2\pi(\theta,\phi)2\pi\sin\theta d\theta$. Since $\rho(0)d\theta=0$ for any $\rho(\theta,\phi)$, one cannot obtain any signals from perfectly aligned molecules as stressed above. Considering the rotational wave function and the probe pulses have the same axial symmetry with respect to $\mathbf{E}$, the relevant component of dipole moment $\mathbf{x}_q(\theta)$ is that parallel to $\mathbf{E}$, $x_q(\theta)$. In fact, the integrated harmonic amplitude in $[\theta, \theta+d\theta]$, $[F_x(\theta)d\theta, F_y(\theta)d\theta, F_z(\theta)d\theta]$ is given by $F_x(\theta)d\theta = x_q(\theta)\rho(\theta)2\pi\sin\theta d\theta$ and $F_y(\theta)d\theta = F_z(\theta)d\theta = 0$. In the present case, there are four characteristic angles [Fig. 3(b)]: At $\theta\sim0$, $F_x(\theta)$ is suppressed due to the symmetry of π_g [$x_q(0)=0$] and geometrical reason [$\rho(0)=0$]. At $\theta\sim\theta_{DI}$, $F_x(\theta)$ is suppressed due to DI and the jump of harmonic phase Θ_{HH} by $\sim\pi$ takes place here [Eq. (1)]. Then, at $\theta\sim\theta_{CI}$, which corresponds to well antialigned molecules in the present case, $F_x(\theta)$ is enhanced due to CI and the large line element $2\pi\sin\theta$. This enhanced $F_x(\theta)$ gives large contributions to the HHG so that harmonic phase is π except for the higher-order harmonics from aligned CO_2. Since θ_{CI} and θ_{DI} are increasing functions of harmonic order q, the positions of DI and CI shift toward $\pi/2$ for higher q. Finally, at $\theta\sim\pi/2$, $F_x(\theta)$ is suppressed due to $x_q(\theta)\sim0$, which is a consequence of π_g symmetry. Now HHG in molecules itself can be regarded as HHG in mixed gases. What one controls by controlling molecular alignment is the difference $\Delta \sim \int^{\theta_{DI}}_0 d\theta F_x(\theta) - \int^{\pi/2}_{\theta_{DI}} d\theta F_x(\theta)$, via manipulating $\rho(\theta)$. $\Delta\sim0$, when the amplitudes of regions I and II are balanced, corresponds to the structure-related minimum and the degree of alignment plays a dominant role for determining the minimum. Finally, the relative phase is the difference between the argument of the weighed mean of $x^{CO_2}_q(\theta)$ and that of x^{Kr}_q as follows:

$$\Delta\Theta_{HH} \sim \arg(\Delta) - \arg(x^{Kr}_q). \tag{6}$$

This coherent character of HHG should be compared to the predicted DI in the above threshold ionization (ATI) process [20]. Although HHG and ATI have similar recollision processes in single atom and/or molecule response, ATI events cannot interfere with each other and each event can be identified by using e.g., COLTRIMS method [21].

In addition to the above fundamental and clear picture, we must consider the effects of phase matching of harmonics, reabsorption of harmonics [12,22], the small difference in I_p between CO_2 and Kr, and the complicated structure of the valence orbital of Kr ($4p$) in order to discuss the relative phase of harmonics. Figure 4 shows the observed (open
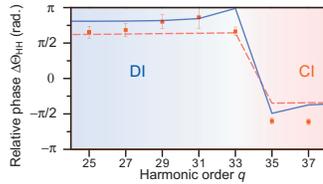
FIG. 4. (Color) The measured (squares) and predicted (dashed line with plane wave functions; thick line with TCC wave functions) relative phases $\Delta\Theta_{HH}$ when CO_2 molecules are aligned ($t_d = 21.2$ ps) as functions of harmonic order q. The relative phase $\Delta\Theta_{HH}$ changes quickly at $q \sim 33$. The gradual increase of both lines except $q \sim 33$ is due to the slight difference in I_p.

squares) and predicted [dashed line from Eq. (6) [23]] relative phases $\Delta\Theta_{HH}$ of the two harmonics at fixed time delays when molecules are aligned ($t_d = 21.2$ ps). The relative phase $\Delta\Theta_{HH}$ changes quickly around $q = 33$, which corresponds to the order where DI takes place, q_{DI}. The position of DI is correctly predicted by Eq. (6), however, there remains a shift between theory and experiment. Such a shift is reported in the numerical solutions for simple two electron systems [16], and we conclude that this is the limitation of the SFA model [6], which cannot describe the recombination dynamics exactly [9]. In fact, the agreement between theory and experiment is improved by using two-center continuum (TCC) wave functions for $|\mathbf{p}\rangle$ (Fig. 4, thick line), which is proposed by Ciappina *et al.* [24] to describe the recombination dynamics correctly. Since harmonic phase is sensitive to the details of theory, measuring phase by the present method will support the quest for the final theory of HHG in molecules [25].

Regardless of such theoretical problems, from $q_{DI} \sim 33$ within the present theory, one can determine the internuclear distance $R^{exp} = 0.242 \pm 0.012$ nm, which is consistent with

the real value $R = 0.232$ nm. Vozzi *et al.* [10] claimed the same $q_{DI} = 33$, however, the present interpretation is somewhat different. While they used the two point emitter model [Eq. (1)] with a dispersion relation $q\omega_0 = (2\pi/\lambda_q)^2/2 + I_p$ and the most probable value $\theta'_{DI} \sim 30°$, we used the exact condition [Eq. (4)] with a dispersion relation $q\omega_0 = (2\pi/\lambda_q)^2/2$ [16] and full angular distribution of molecules. For more highly aligned molecules, q_{DI} should take lower values (e.g., $q_{DI} \sim 27$ in Ref. [8]). Furthermore, by using the observed phase jump, it is possible to control the pulse duration of harmonics coherently. Considering the attochirp of the reference harmonics from Kr is relatively small, the observed jump of relative phase indicates that the attochirp of harmonics from CO_2 is enhanced around DI. Therefore if one superposes harmonics with DI regions (e.g., 25th–37th at $t_d = 21.2$ ps), the pulse duration of the harmonics should be rather long compared to the harmonics without DI regions (e.g., 35th–37th), where the dominant chirp is the ordinal attochirp just like atomic cases [1,4]. Finally, q_{DI} can be controlled by manipulating the degree of alignment, i.e., by changing the intensity and duration of pump pulses [8,10].

Using mixed gases as nonlinear media for HHG offers us a new route not only to observe underlying physical processes of HHG in atoms and molecules but also to control HHG coherently. Furthermore, from the R dependence of the dipole moment in Eq. (3), harmonic phases are expected to be sensitive to the size of molecules in general and through the measurement of them it may be possible to observe the structures of larger systems such as biological molecules. The other story of HHG has just begun.

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