

## Laser intensity dependence of high-order harmonic generation from aligned CO<sub>2</sub> molecules

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We investigate experimentally the high-order harmonic generation from aligned CO<sub>2</sub> molecules and demonstrate that the modulation inversion of the harmonic yield with respect to molecular alignment can be altered dramatically by fine-tuning the intensity of the driving laser pulse for harmonic generation. The results can be modeled by employing the strong field approximation including a ground state depletion factor. The laser intensity is thus proved to be a parameter that can control the high-harmonic emission from aligned molecules.

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High-order harmonic generation (HHG) from atoms and molecules has been one of the most intensively explored topics in high-field laser physics, due to its application in producing ultrafast coherent extreme ultraviolet (xuv) radiation and even attosecond pulses [1–3]. In the strong field limit, HHG is well explained by a three-step model: active electrons first tunnel through the potential barrier, are accelerated by laser fields, and then recombine with parent ions to emit high-energy photons [4]. The fast-moving electrons in the HHG process provide opportunities to probe electronic and nuclear dynamics of atoms and molecules with unprecedentedly short time resolution. Based on the underlying physics of HHG, recent experimental studies succeeded in not only taking tomographic images of the highest occupied molecular orbital (HOMO) of the nitrogen molecule [5] but also probing proton motions of hydrogen and methane molecules with subfemtosecond time resolution [6], showing the potential application of the harmonic generation process.

On the other hand, owing to the additional degrees of freedom, i.e., rotational and vibrational motions, molecules offer extra parameters as useful tools to control the HHG characteristics [7,8]. Through nonadiabatic alignment imposed by a short laser pulse kick, molecules are partially aligned along or perpendicular to the laser polarization direction at different delay times due to the evolution of the excited rotational wave packet [9]. As a result, the harmonic emission is modulated in time. It has been shown by Itatani *et al.* [8] that HHG from such impulsively aligned molecules (O<sub>2</sub>, N<sub>2</sub>) is dependent on the angle  $\theta$  between the aligned molecular axis and the polarization of the driving laser field, e.g., the harmonics generated from the O<sub>2</sub> molecule are enhanced when aligned near 45° with respect to the laser polarization, due to the  $\pi_g$  symmetry of its HOMO, while for N<sub>2</sub> (with  $\sigma_g$  symmetry of the HOMO), harmonic emission is the strongest when the molecule is aligned along the polarization direction. For larger polyatomic molecules such as acetylene (HC≡CH) and allene (H<sub>2</sub>C=C=CH<sub>2</sub>), where the HOMO has  $\pi_u$  symmetry, the harmonic yield is reversely modulated by the molecular alignment [10]. This angle dependence of the harmonics with respect to molecular align-

ment offers a potential way of shaping HHG and attosecond pulses.

HHG from CO<sub>2</sub> presents an interesting additional feature of the molecular alignment dependence. As shown by Kanai *et al.* [11], the harmonic yields for the 17th–29th orders from aligned CO<sub>2</sub> molecules exhibit *inverted* modulation versus the field ionization and alignment parameter  $\langle \cos^2 \theta \rangle$ . This modulation inversion was attributed to the interference of recombination electrons from the two oxygen atoms in the CO<sub>2</sub> molecule. Vozzi *et al.* [12] reported further that the two-center interference effect can be controlled by changing the ellipticity of the driving laser pulse. They showed that the inverted modulation of the harmonic signal appears for the 21st–39th harmonic orders, while the modulation of the harmonic emission of the 41st–49th orders is the same as the molecular alignment. The difference in harmonic orders with inverted modulation cannot be explained by constructive and destructive interference. By taking into account the ground state depletion effect on HHG, Le *et al.* [13,14] recently proposed theoretically that the harmonic yield inversion can be varied by changing the driving laser intensity. This may explain the inversion for different harmonic orders, but an experimental verification of this model is strongly desired.

In order to explore the underlying physics in the angular dependence of high-harmonic emission from aligned molecules, we investigate the HHG from aligned CO<sub>2</sub> molecules as a function of the driving laser intensity in this work. We observed that, on changing the laser intensity, the modulation of harmonic yield from aligned molecules can be varied and even inverted with respect to the molecular alignment. Our experimental results are compared with the numerical calculations employing the strong field approximation model including the ground state depletion effect. The role of laser intensity as a parameter to control the angular dependence of HHG in aligned molecules is revealed.

Our experiments were performed using a Ti:sapphire-based chirped pulse amplification laser system (Spectral-Physics, TSA-25), which produces 50 fs laser pulses of 10 Hz at 800 nm center wavelength. The output is split into two beams, one used as the pump pulse (for aligning molecules) and the other as the probe pulse (for driving HHG from the molecules). The polarization of the pump laser beam is the same as the probe beam. The two beams were collinearly focused with a 30 cm focal length lens onto a pulsed supersonic molecular beam located in a high-vacuum interaction

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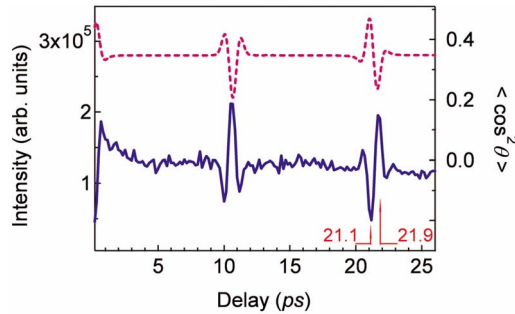


FIG. 1. (Color online) Measured 23rd harmonic yield (solid line) from aligned  $\text{CO}_2$  molecules and calculated alignment parameter  $\langle \cos^2 \theta \rangle$  (dashed line) as functions of the pump-probe delay time. The temporal modulation of the harmonic intensity reverse-matches the alignment.

chamber. The laser focus was about 1 mm downstream of a 0.25-mm-diameter nozzle orifice. The stagnation pressure of  $\text{CO}_2$  gas (99.998%) was around 2 bars, leading to a rotational temperature of several tens of kelvins. The spot size of the pump laser beam crossing with the molecules was measured to be  $110 \mu\text{m}$  [full width at half maximum (FWHM)] and the laser field intensity was estimated to be  $2.1 \times 10^{13} \text{ W/cm}^2$ . The probe laser energy was adjustable by using a half-wave plate and a high-extinction film polarizer. At the interaction position, the spot size of the probe beam was measured to be  $144 \mu\text{m}$  (FWHM). The HHG spectra were detected by a homemade flat-field grating spectrometer equipped with a soft-x-ray charge-coupled device camera (Princeton Instruments SX 400).

When a  $\text{CO}_2$  molecule is irradiated by a short laser pulse whose duration ( $\tau_{\text{on}}=50$  fs) is much shorter than the molecular rotational period,  $\tau_{\text{on}} \ll 2\pi/\omega=42.7$  ps for  $\text{CO}_2$ , nonadiabatic field-free alignment is achieved by the excitation of a rotational wave packet  $\psi(t)=\sum_{J,M} A_{J,M}(t)|J,M\rangle$  [9,15,16]. The time evolution of the wave packet can be calculated through solving the time-dependent Schrödinger equation (TDSE) and the time-dependent alignment parameter  $\langle \cos^2 \theta \rangle(t)$  is defined as  $\langle \cos^2 \theta \rangle(t)=\langle \psi(t)|\cos^2 \theta|\psi(t)\rangle$ . In our calculation the initial rotational temperature is taken to be 80 K and the result is shown in Fig. 1 (dashed line, right axis).

The experimentally measured 23rd harmonic intensity as a function of pump-probe delay time is also represented in Fig. 1 (solid line, left axis). The probe laser intensity was  $2.4 \times 10^{14} \text{ W/cm}^2$ . It is evident that the modulation of the harmonic signal is reverse-matched with that of the molecular alignment parameter  $\langle \cos^2 \theta \rangle$  exactly. This is consistent with the experimental results of Kanai *et al.* [11] and Vozzi *et al.* [12] that the harmonic signal reverse-matches the alignment parameter  $\langle \cos^2 \theta \rangle$ . The phenomenon was regarded as evidence of the interference of the recombining electrons originating from two oxygen atoms.

In Fig. 2(a) we plot the measured harmonic intensities for the 17th–31st order harmonics at two pump-probe delays 21.1 and 21.9 ps, obtained with a probe laser intensity of  $2.4 \times 10^{14} \text{ W/cm}^2$ . The harmonic intensity is normalized to that of an isotropic distribution of  $\text{CO}_2$  molecules (without using the pump laser pulses). As labeled in Fig. 1, the delay

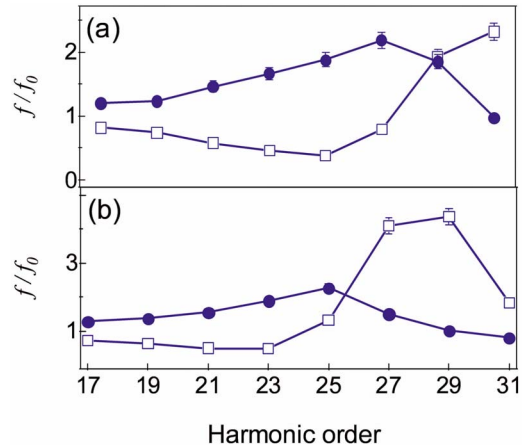


FIG. 2. (Color online) Normalized harmonic intensities ( $f/f_0$ ) for the 17th–31st order harmonics at two pump-probe delays: 21.1 (open squares) and 21.9 ps (solid circles) for two probe laser intensities: (a)  $2.4 \times 10^{14}$  and (b)  $1.9 \times 10^{14} \text{ W/cm}^2$ . The harmonic intensity is normalized to that of an isotropic distribution of  $\text{CO}_2$  (without using the pump laser pulses) subjected to the same probe laser field. With the higher probe laser intensity (a), the 17th–27th harmonic signals at 21.1 ps are weaker than those at 21.9 ps (inverted with respect to molecular alignment). When the probe laser intensity decreases to  $1.9 \times 10^{14} \text{ W/cm}^2$ , the reversed harmonic orders are the 17th–25th orders.

time 21.1 ps corresponds to the alignment condition when molecules are mostly aligned along the laser polarization direction, while 21.9 ps corresponds to the perpendicular alignment case. As one can see, the harmonic emissions are inverted with respect to molecular alignment  $\langle \cos^2 \theta \rangle$  for the 17th–27th orders. In Fig. 2(b) we show that, on decreasing the probe laser intensity to  $1.9 \times 10^{14} \text{ W/cm}^2$ , the intensity-reversed harmonics at 21.1 and 21.9 ps pump-probe delays change to the 17th–25th orders.

This experimental result is interesting in light of the fact that the two-center interference effect is determined only by the alignment angle and the de Broglie wavelength of recombining electrons. As Le *et al.* have shown in the calculation [13], the 33rd harmonic intensity has a reversed modulation compared to that of the molecular alignment at the driving laser intensity of  $2 \times 10^{14} \text{ W/cm}^2$ , and it changes to be the same as that of the molecular alignment when the laser intensity decreases to  $1 \times 10^{14} \text{ W/cm}^2$ . Although in our experiments the 33rd harmonic is too weak to be distinguished, the results shown in Fig. 2 are in principle consistent with the calculated results [13,14].

For further investigation of the laser intensity dependence of harmonic emission from aligned molecules, we measured the 25th harmonic yield at around half the revival of molecular alignment under four different probe laser intensities:  $1.6 \times 10^{14}$ ,  $1.9 \times 10^{14}$ ,  $2.1 \times 10^{14}$ , and  $2.4 \times 10^{14} \text{ W/cm}^2$ . The results are shown in Figs. 3(a), 3(b), 3(c), and 3(d), respectively. As we can see, the modulation of the 25th order harmonic yield is completely inverted as the laser intensity increases to  $2.1 \times 10^{14} \text{ W/cm}^2$  [Fig. 3(c)] and the inversion can survive at a higher intensity of  $2.4 \times 10^{14} \text{ W/cm}^2$ . It should be noted that the change in probe laser intensity does not induce significant variation of the molecular alignment

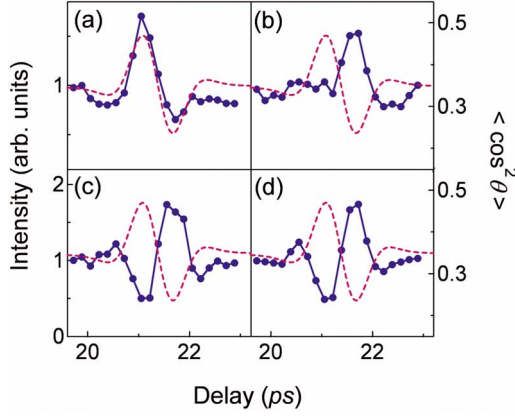


FIG. 3. (Color online) Time evolution of the 25th order harmonic intensity from aligned CO<sub>2</sub> at around half revival for the probe laser intensities of (a)  $1.6 \times 10^{14}$ , (b)  $1.9 \times 10^{14}$ , (c)  $2.1 \times 10^{14}$ , and (d)  $2.4 \times 10^{14}$  W/cm<sup>2</sup>. Also shown is the calculated alignment parameter  $\langle \cos^2 \theta \rangle$  (dashed line).

during the HHG process. We thus demonstrate that the angular dependence of harmonic emission with respect to molecular alignment can be varied dramatically and even inverted by tuning the probe laser intensity.

In order to clarify the role of the laser field intensity, we performed numerical simulations using an extended Lewenstein strong field approximation model [17] including the ground state ionization effect. In this model, the harmonic spectrum from molecular dipole moment in the time domain is calculated by using

$$\mathbf{x}(t) = i \int_0^\infty d\tau \left( \frac{\pi}{\epsilon + i\tau/2} \right)^{3/2} \mathbf{d}^*[\mathbf{p}_{\text{st}} - \mathbf{A}(t)] e^{-iS(\mathbf{p}_{\text{st}}, t, \tau)} \times \mathbf{E}(t - \tau) \cdot \mathbf{d}[\mathbf{p}_{\text{st}} - \mathbf{A}(t - \tau)] a^*(t) a(t - \tau) + \text{c.c.}, \quad (1)$$

where  $\mathbf{d}^*[\mathbf{p}_{\text{st}} - \mathbf{A}(t)]$  and  $\mathbf{d}[\mathbf{p}_{\text{st}} - \mathbf{A}(t - \tau)]$  are the transition dipole moments between the ground state and the continuum state,  $\mathbf{p}_{\text{st}} = \int_{t-\tau}^t \mathbf{A}(t') dt' / \tau$  is the canonical momentum at the stationary points with vector potential  $\mathbf{A}$ , and the exponential term takes account of the action of the electron trajectories within the laser field. We consider the depletion of ground state molecules by a factor of  $a(t)$ , which is approximated by  $a(t) = \exp[-\int_{-\infty}^t dt' W(t')/2]$  [13], and  $W(t')$  is the tunneling ionization rate obtained by molecular orbital Ammosov-Delone-Krainov (ADK) theory [18].

To calculate the transition dipole moments the ground state of CO<sub>2</sub> is expressed using the atomic  $2p_y$  orbital  $\Phi_{2p_y}$  as [19–21]

$$\Psi_{\pi_g}(\mathbf{x}) \propto [\Phi_{2p_y}(\mathbf{x} + \mathbf{R}/2) - \Phi_{2p_y}(\mathbf{x} - \mathbf{R}/2)], \quad (2)$$

where  $R$  is the distance between oxygen atoms, and the  $2p_y$  orbital is expressed by an  $\sim \exp(-\alpha|x|)$ -type basis function. The time-dependent dipole transition moment is given by

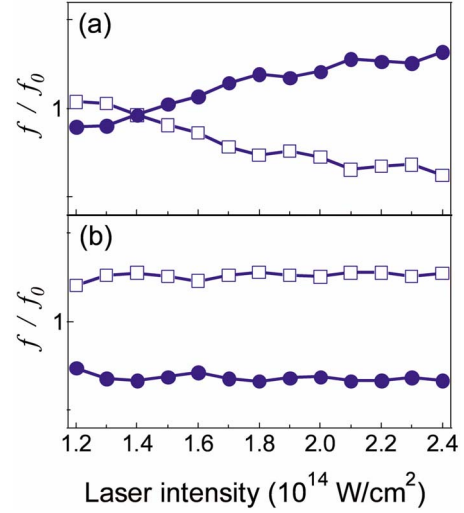


FIG. 4. (Color online) Calculated normalized intensities ( $f/f_0$ ) of the 25th order harmonic emission at two pump-probe delays: 21.1 (open squares) and 21.9 ps (solid circles) as functions of the probe laser intensities from  $1.2 \times 10^{14}$  to  $2.4 \times 10^{14}$  W/cm<sup>2</sup>. The calculations were carried out by (a) considering and (b) not considering the ground state depletion factor.

$$\mathbf{d}_{\pi_g}(\mathbf{p}) \propto [2i \sin(\mathbf{p} \cdot \mathbf{R}/2) d_{2p_y}(\mathbf{p}) - \cos(\mathbf{p} \cdot \mathbf{R}/2) \tilde{\Phi}_{2p_y}(\mathbf{p}) \mathbf{R}], \quad (3)$$

in which  $d_{2p_y}(\mathbf{p})$  is the atomic dipole moment from the  $2p_y$  orbital and  $\tilde{\Phi}_{2p_y}(\mathbf{p})$  is the  $2p_y$  wave function in the momentum space. Finally, the harmonic spectra as a function of the angle between molecular axis and laser polarization,  $S(\theta)$ , are obtained through the Fourier transform of the transition dipole moment.

In order to calculate the harmonic intensities from aligned CO<sub>2</sub> molecules, the time-dependent alignment distribution of molecules has to be taken into account. At the field-free evolution time  $t$ , the distribution of aligned molecular axis is expressed as  $P(\theta, t) = |\langle \psi(t) | \psi(t) \rangle|^2$ , in which  $\psi(t)$  is obtained by solving the TDSE. The harmonic intensity evolution is given by integrating the product of  $S(\theta)$  and  $P(\theta, t)$ ,

$$f(t) \propto \int S(\theta) P(\theta, t) \sin \theta d\theta. \quad (4)$$

To compare with the experimental results, we first calculate the angular distribution  $S(\theta)$  of the 25th harmonics using different driving laser intensities from  $1.2 \times 10^{14}$  to  $2.4 \times 10^{14}$  W/cm<sup>2</sup>. The molecular alignment distributions  $P(\theta, t=21.1 \text{ ps})$  and  $P(\theta, t=21.9 \text{ ps})$  are obtained from  $\psi(t)$  by solving the TDSE using the experimental conditions. At these two delay times, the CO<sub>2</sub> molecules are mostly aligned along the laser polarization direction ( $\theta=0^\circ$ ) and perpendicular to the laser polarization ( $\theta=90^\circ$ ), respectively. Based on Eq. (4) the calculated harmonic yields of  $f(t=21.1 \text{ ps})$  and  $f(t=21.9 \text{ ps})$  are normalized and plotted in Fig. 4(a). It is evident that the harmonic yields are clearly modulated by the laser intensity. With the laser intensity in the range from  $2.4 \times 10^{14}$  to  $1.4 \times 10^{14}$  W/cm<sup>2</sup>, the normal-

ized 25th order harmonic intensity at  $t=21.9$  ps is stronger than at  $t=21.1$  ps (i.e., the harmonic intensity modulation is inverted with the molecular alignment). When the laser intensity decreases to  $1.4 \times 10^{14}$  W/cm<sup>2</sup> and lower, the harmonic intensities at the two delays are reversed back to match the modulation of molecular alignment. The calculated results reproduce well the experimental results shown in Fig. 3, except for a small difference in the absolute value of laser intensity where the inversion starts to occur. A more rigid model for the HHG in CO<sub>2</sub> may help to reduce this quantitative difference between the experimental and calculated results.

For comparison, we also calculate the harmonic intensities  $f(t=21.1$  ps) and  $f(t=21.9$  ps) without including the ground state depletion factor  $a(t)$ , and the results are shown in Fig. 4(b). It is shown that the normalized harmonic signals at  $t=21.1$  ps (the molecules are aligned with the laser polarization direction) are stronger than those at  $t=21.9$  ps (the antialigned case) in the whole range of different probe laser intensities. However, in the experimental results shown in Fig. 3 we observed this modulation only when the laser field intensity is reduced to  $1.6 \times 10^{14}$  W/cm<sup>2</sup>. Clearly, the calculation without considering the ground state depletion cannot reproduce the experimental observation of the intensity modulation inversion of the 25th order harmonic. The above calculated results indicate the necessity of including the ground state depletion factor into the strong field approximation model in the calculation of harmonic emission from aligned molecules.

The above analysis indicates that ground state depletion might be an important factor responsible for the observed

laser intensity dependence of the angular distribution of harmonic emission from aligned molecules. However, a further investigation is still necessary to understand how the probe laser intensity affects the HHG from aligned molecules.

From Eq. (4) we know that to control the angular distribution of HHG one could also adjust the molecular alignment distribution  $P(\theta)$ . The recent progress in three-dimensional alignment of molecules [22–24] is expected to play a role in controlling HHG. Experiments on higher-order harmonics with finely adjusted driving laser intensity may lead to a more comprehensive understanding of the angular dependence of harmonics and therefore a better control of HHG.

In conclusion, we experimentally demonstrate that the harmonic emission from aligned CO<sub>2</sub> molecules as a function of alignment angle can be altered dramatically by fine-tuning the intensity of the driving laser pulses. The experimental results can be modeled by the strong field approximation model including the ground state depletion effect. The laser intensity is thus proved to be a parameter that can be used to control the high-harmonic emission from aligned molecules.

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