Measurement of the angular distributions of high-order harmonic generations from aligned CO$_2$

H Lu, S T Zhao, Z X Zhang, P Liu, Z N Zeng, R X Li, and Z Z Xu
Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, No. 390, Qinghe Road, Jiading District, Shanghai 201800, China

E-mail: peng@siom.ac.cn, ruxinli@mail.shcnc.ac.cn

Abstract: In this study, the angular distributions of harmonics emission from aligned CO$_2$ are explored experimentally and theoretically, and the validity of Strong Field Approximation (SFA) model in the molecular high harmonic generation is therefore studied. The study shows that for describing the angle distribution of high harmonic generation from molecules, SFA is roughly consistent with the qualitative analysis, while the quantitative analysis is different.

High-order harmonic generation (HHG) from molecules attracts much attention due to the increased freedom of molecules that reveals a rich set of phenomena[1-6]. In the well understood three-step process[7-9], in which the tunneling ionized electrons are accelerated by the strong laser field and then return to combine with the parent ions to eject high energy photons, the ionization and recombination steps are all dependent on the symmetry of the highest occupied molecular orbital (HOMO) of molecules[10,11]. Consequently, the harmonic emission from molecules irradiated by strong laser field shows angle dependence between the molecular axis and laser polarization direction[12]. This feature provides a means to shape the characteristics of harmonic emissions. The recent measurement of polarization state of harmonic emission from N$_2$, O$_2$ and CO$_2$ molecules shows a strong dependence on the molecular alignment and the orbital structures[13].

Moreover, the HHG from molecules shows potential application in probing molecular dynamics. From an ensemble of aligned nitrogen molecules, the harmonic intensities as a function of the angle $\theta$ between molecular axis and laser polarization is able to be utilized to rebuild the tomographic image of the highest occupied molecular orbital (HOMO) [14]. The recent measurement of high harmonic generation from aligned organic molecules[15] shows the imaging method can also extend to more complex molecules based on the validity of strong field approximation (SFA). This shows the potential application of harmonic generation process in extracting the molecular structure information from the angle distribution of harmonic emissions.

The structural retrieval is also possible by examining the quantum interference signatures in spectrum measurement. The CO$_2$ molecule provides good conditions for observing the quantum interference in harmonic generation, due to its characteristic linear structure. Its highest occupied molecular orbital (HOMO) is an antisymmetric $\pi_{\text{g}}$ orbital dominated by the combination of the $\text{p}_{\text{y}}$ orbitals of the two oxygen atoms, and the O - O distance ($R_{\text{O} - \text{O}} = 0.232$ nm) corresponds to an electron wavelength typical of the harmonic generation process. According to the two-center interference model[16,17], destructive interference appears as $R \cos \theta = n \lambda_{\text{e}}$, where $R$ is the distance of the two ionization sites that reveals the bond length of molecule, $\theta$ is the angle of molecular axis and $n$ is the harmonic order.
electron momentum, and \( n \lambda_e \) is the integer times of electron de Broglie wavelength. Since the molecules are partially aligned in experiments and harmonic emission from molecules are \( \theta \) dependent, one needs take into account not only the alignment distribution of molecules, \( P(\theta) \), but also the harmonic intensity distributions, \( S(\theta) \), in order to investigate the quantum interference effect.

Therefore, the angle dependence of harmonic emission - \( S(\theta) \) - plays a key role in the study of probing molecular structures and shaping high harmonic emissions. Accurate measurement of the angle distributions of harmonics and theoretical apprehension are critical steps towards the tomographic imaging technique for larger molecules such as CO\(_2\). So far the angle dependence for CO\(_2\) molecule has not been measured directly yet and the comparison of SFA calculation with experimental observations is needed.

In this study we investigate the angular distributions of harmonics produced for aligned CO\(_2\) molecules experimentally and theoretically. The calculated result by SFA agrees the experimental results qualitatively. From numerical simulations, the angular profiles of the harmonic emission have been discussed.

Due to the limit of partially aligned molecules, the angle distribution \( S(\theta) \) in molecular frame can not be measured directly. Experimentally we can only measure the harmonic intensities as a function of the angle \( \Theta \) between pump laser polarization and probe laser polarization in laboratory frame. Our experiment was performed using a Ti:sapphire based chirped pulse amplification laser system (Spectral-Physics, TSA-25), which produce 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 molecules). The polarization of the pump laser beam is fixed as p polarization state, while the probe beam polarization is adjusted by a zero-order air filled wave plate from s to p state. The two beams are combined by a normal incidence beam splitter in the angle of \(< 3^\circ\) and then were collinearly focused (with a 30 cm focal length lens) onto a pulsed supersonic molecular beam located in a high vacuum interaction chamber. The laser focus was about 1 mm downstream of a 0.25 mm diameter nozzle orifice. Stagnation pressure of CO\(_2\) gas (99.998%) was 2 bars. Through the calculation to a rotational temperature of several tens of Kelvin. The HHG spectra were detected by a home-made flat-field grating spectrometer equipped with a soft-x-ray CCD camera (Princeton Instruments, PI: SX 400).

First the CO\(_2\) molecules are first aligned in an optimized condition. The highest alignment degree \( \langle \cos^2 \theta \rangle \) is normally improved by increasing the pump laser pulse energy, but the applied laser pulse energy is limited by the ionization due to increased laser intensity. In experiments we tune the laser field just below the value that produces detectable high harmonics. The field intensity is estimated to be \( 4 \times 10^{13} \) W/cm\(^2\). The intensity of the 23\(^{th}\) harmonic as a function of the delay time after pump pulse is shown in figure 1(a) (solid line). As can be seen the alignment revivals are achieved at the full, half, quarter of molecular rotational period. Under the experimental conditions, the pump laser pulse duration (\( \tau_{\text{on}} = 50 \) fs) is much shorter than the molecular rotational period, \( \tau_{\text{on}} < 2 \pi / \omega = 42.7 \) ps for CO\(_2\), nonadiabatic field-free alignment is achieved by the excitation of a rotational wavepacket \( \psi(t) = \sum_{J,M} A_{J,M}(t) |J,M\rangle \) \[18-20\]. The time evolution of the wavepacket can be calculated through solving the time-dependent Schrödinger equation (TDSE). The time dependent alignment parameter defined as \( \langle \cos^2 \theta \rangle(t) = \langle \psi(t) | \cos^2 \theta | \psi(t) \rangle \) is calculated shown in figure 1(a) (dashed line, right axis). In our calculation the initial rotational temperature is taken to be 80 K estimated based jet kinetic models. It is evident that the modulation of harmonic signal is reversely matched with that of the molecular alignment parameters \( \langle \cos^2 \theta \rangle \) exactly. This is consistent with the experimental results of Kanai et al. [11] and Vozzi et al. [21] that reveals quantum interference effect.

At the delay time \( t = 21.1 \) ps where CO\(_2\) are aligned at the half revival, harmonic spectra are recorded by tuning the angle \( \Theta \) between pump laser polarization and probe laser polarization from 0\(^{\circ}\)
to 90°. Harmonic spectra are also taken by only introducing probe laser pulse, which generates the harmonic emission from isotropic molecules. The ratios of harmonic intensities (the 19th, 23rd, and 27th harmonic) from aligned and isotropic molecules are plotted in figure 1(b). It is seen that for all the observed harmonics, the normalized intensities all increase from a value lower than 1 at Θ = 0° to larger than 1 at Θ = 90°. This is the inversion of the harmonic emission resulted from quantum interference effect, which is consistent with the previous report. It is also noted that the slopes of the increasing harmonic intensity is larger when the harmonic order is larger, for the 19th harmonic emission, the normalized intensity increase from 0.65 to 1.1, while for the 27th harmonics, the intensity increase from 0.3 to 1.4. Since the molecular alignment distribution is fixed, this indicates the variation of angle dependence of harmonic emission S(θ) for the observed harmonic orders.

Figure 1. (a) Measured 23rd harmonic yield (solid line, left axis) and calculated alignment parameter <cos^2 θ > (dashed line, right axis) as functions of the pump-probe delay time; (b) the ratio of harmonic intensities (19th, 23th, 27th harmonic) from aligned and isotropic molecules.

The measured angular dependence in laboratory frame is related to the angular dependence of harmonic generation by

\[
I_n(\Theta) = \int \left[ \tilde{R}P(\theta) \cdot \tilde{R}S(\theta) \right]^2 d\omega
\]

where P(θ) is the alignment distribution of the molecular axis in molecular frame, S(θ) is the amplitude and phase part of the harmonic emission, and \( \tilde{R} \) is the rotation operator that transform the distribution function in molecular frame to laboratory frame, which includes a rotation of polar angle θ and a integral of azimuthal angle χ. To simulate the measured result, P(θ) and S(θ) need be evaluated, then the harmonic intensities are calculated from Eq. (1) and finally the intensities are normalized by calculated harmonic emission from an isotropic ensemble of molecules.

In order to simulate the experimental results, we use the Lewenstein’s strong field approximation model [22] to calculate the angular distribution S(θ). In the model, the harmonic spectrum from molecular dipole moment in the time domain is calculated by using

\[
x(t) = \int d(t - \tau) e^{i\omega(t - \tau)} dp \left[ p - A(t) \right] e^{-iS(p,t)}
\]

\[
\times E(t - \tau) \cdot d[p - A(t - \tau)] \times a^\dagger(t) a(t - \tau) + c.c.
\]

where \( d[p - A(t)] \) and \( d[p - A(t - \tau)] \) are the transition dipole moments between the ground state and the continuum state, \( p = \int_{-\tau}^{\tau} A(t')dt'/\tau \) is the canonical momentum at the stationary points with vector potential 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 
\[
a(t) = \exp\left[-\int_{-\infty}^{t} dt' W(t') / 2 \right] \quad [23],
\]
and \( W(t') \) is the tunneling ionization rate obtained by MO-ADK theory \([24]\).

To calculate the transition dipole moments the ground state of \( \text{CO}_2 \) is expressed by atomic \( 2p_y \) orbital \( \Phi_{2p_y} \) as \([25-27]\)
\[
\Psi_{\pi_e}(x) \propto \left[ \Phi_{2p_y}(x + R/2) - \Phi_{2p_y}(x - R/2) \right],
\]
where \( R \) is the distance between oxygen atoms, and the \( 2p_y \) orbital was expressed by
\[
\sim \exp(-\alpha|x|) \text{type basis function.}
\]
The time dependent dipole transition moment is given by
\[
d_{\pi_e}(p) \propto [2i \sin(p \cdot R/2) d_{2p_y}(p) - \cos(p \cdot R/2) \Phi_{2p_y}(p) R],
\]
in which the \( d_{2p_y}(p) \) is the atomic dipole moment from the \( 2p_y \) orbital and \( \Phi_{2p_y}(p) \) is the \( 2p_y \) wavefunction 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.

The time-dependent alignment distribution of molecules \( P(\theta, t = 21.1\, \text{ps}) \) is calculated from the \( \psi(t) \) by solving the TDSE. The \( \Theta \) dependence of harmonic intensity is then given by integrating the product of \( S(\theta) \) and \( P(\theta) \) as Eq. (1).

The calculated \( \Theta \) dependence of 19th to 27th harmonics is plotted in figure 2(a). It can be seen that, the calculated harmonic intensities represent the same major features as observed in experiments. From \( \Theta = 0^\circ \) to \( \Theta = 90^\circ \) the intensities all increases from a value less than 1 to one larger, and the 27th harmonic emission has the largest increase while the 19th harmonic emission has the lest increment. The consistence shows the calculation of angle distribution \( S(\theta) \) by SFA agrees with the observation generally.

![Figure 2](image)

**Figure 2.** (a) The calculated \( \Theta \) dependence of the normalized harmonic intensities for 19th, 23rd and 27th harmonics; (b) the calculated angle distribution \( S(\theta) \) of 19th, 23rd and 27th harmonics.

In figure 2(b) the calculated angle distribution \( S(\theta) \) of 19th, 23rd, and 27th harmonics are shown. Evidently the 19th harmonic emission has a broader angle distribution than the others and it is the different angle distributions that result in the change of \( \Theta \) dependence for harmonic orders.

It is also noted that in figure 2(a), the values of normalized harmonic intensities does not match with the experimental results, the 19th, 23rd and 27th harmonic emission are all between 0.5 – 0.6 for \( \Theta \)
= 0°, and they increase to 1.2 – 1.3 for Θ = 90°. One possibility is the uncertainty of estimated rotational temperature. To clarify the influence of temperature, we calculate the Θ dependence of harmonic intensities for an ensemble of aligned molecules at 120K. The normalized intensities are all within 0.6 – 0.7 for Θ = 0°, and increases to around 1.2 for Θ = 90°. This means the rotational temperature of molecules is not a critical influence of the inconsistence of experimental and calculated results.

To further discuss how the angle distribution $S(\theta)$ influences the observed Θ distribution of harmonic intensities, we carry out the following simulations. We assume the profile of $S(\theta)$ as a Gaussian function that is centered at 66° (about the peak positions calculated by SFA), then calculate the Θ distributions by set the full width at the half maximum (FWHM) of the function from 10° to 50° with a step size of 10°. The result is shown in figure 3(a), which shows that at Θ = 0° the harmonic intensity decreases to 0.5 by using a FWHM of 10°. In our second simulation, we choose the FWHM of Gaussian function as 20° and change the peak positions of $S(\theta)$ from 50° to 90° with a step size of 10°. The calculated Θ distributions of harmonic intensities are plotted in figure 3(b). As can be seen, when the peak position of $S(\theta)$ in molecular frame shift from 60° to 90°, the resulted harmonic emission changes from 0.6 to 0.3 for Θ = 0°. This shows that, the peak position and width of angle distribution $S(\theta)$ both significantly influence the Θ distributions of harmonic intensities in laboratory frame. By the peak position located at near 90°, the harmonic emission decreases to be about 0.3 for Θ = 0°, as observed in experiments for the 27th harmonics.

![Figure 3](image-url)  
**Figure 3.** (a) The dependence of the normalized harmonic intensities for 19th, 23rd and 27th harmonics on the harmonic angle distribution $S(\theta)$: (a) dependence on the profile width; (b) dependence on the profile center.

The above analysis indicates that SFA is roughly consistent with the qualitative analysis but the quantitative analysis is different. The recent progress in tomographic imaging of molecular orbitals[28,29] shows that besides HOMO contribution to HHG, the lower bounds HOMO-n may also play a part in the process, which may lead to deviation of experimental results from calculation results from SFA. While this holds true for N2, for CO2, the conclusion is not settled yet.

In conclusion, we investigated experimentally the angular distributions of high harmonic generation from aligned CO2 molecules by tuning the angle between pump laser polarization and probe laser polarization from 0° to 90° while fixing the pump-probe delay time at the half revival of alignment. Although the calculated results by Strong Field Approximation (SFA) under the same conditions agree with the experimental results qualitatively, further discussion on the quantity difference between experimental results and calculation results indicate that modification is needed in
the SFA model for accurate description of angle distribution \( S(\theta) \).

This work is supported by Chinese Academy of Science, Chinese Ministry of Science and Technology, NSF of China (Grant Nos. 10734080, 10523003, 60921004, and 60978012), 973 Program of China (2006CB806000), and Shanghai Commission of Science and Technology (Nos. 06DZ22015 and 07pj14091).

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