

Role of orbital symmetry in high-order harmonic generation from aligned molecules

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(Received 28 October 2003; published 17 March 2004)

High-order harmonic generation has been explored theoretically and experimentally in CO₂, a linear molecule characterized by doubly antisymmetric highest-occupied molecular orbitals. For the first time to our knowledge, the high-harmonic yield is studied as a function of the angle between the molecular axis and the polarization direction. A minimum yield is found at 0° for all harmonics, which constitutes evidence for destructively interfering terms in the ionization probability amplitude playing an important role in strong-field phenomena in molecules. The maximum yield is always found at intermediate angles, but the detailed behavior is harmonic specific. Numerical simulations reproduce the main features observed in the experiment.

DOI: 10.1103/PhysRevA.69.031804

PACS number(s): 42.65.Ky, 42.50.Hz, 33.80.Wz, 34.50.Gb

Strong-field interactions with molecules are not as well understood as for atoms. In atoms, both fully quantum-mechanical calculations [1–4] and semiclassical models [5,6] reproduce single-electron ionization and related phenomena—high-harmonic generation (HHG) and above-threshold ionization (ATI)—with good accuracy. In contrast, for many molecules there is now consistent experimental evidence indicating that ionization rates are significantly lower than those in atoms with the same ionization potential (IP) [7–10].

In order to understand the reduced ionization, several theoretical approaches have been applied in an attempt to include molecular effects like vibrations [11] or multicenter potentials [12]. However, attaining quantitative agreement in the magnitude of the ionization suppression, while at the same time explaining why the phenomenon occurs only in some molecules (O₂, H₂, D₂, etc.) but not all (N₂ behaves exactly like its companion atom Ar), has proven elusive. A recent calculation [13] extended the tunneling ionization model of Ammosov-Delone-Krainov (ADK) [14] to account for the differences in the electronic wave functions of atoms and molecules. Together with a correct prediction of the extension of the HHG cutoff in oxygen [15], modeled ratios of ionization of several species with respect to their companion atoms are compatible with experiment, the main discrepancy occurring for F₂. An alternative method was suggested by Muth-Böhm *et al.* [16,17]. They modified the intense-field many-body *S*-matrix theory, initially developed for atoms, to include an interference term due to electron waves emitted in different positions in space. Their results indicated that the ionization probability of a molecule would never exceed that of an atom of similar IP, since the multicentered character of the potential would necessarily cause some degree of destructive interference. Once again, the model has partial, species dependent success. Related ideas have also proven useful to describe molecular ATI spectra [18].

Other studies have shown that the symmetry of the electron wave function also influences processes involving recollision of the tunnel-ionized electron, leading to anomalous ellipticity dependences [19,20]. For linear polarization, recollision is expected to be suppressed when the field points along a nodal plane, since the symmetry imposes a transverse drift of the electron away from the polarization axis.

A related effect was discussed in Refs. [21,22], where it was found that, for processes involving electron recollision, interference would necessarily occur in molecules due to the presence of several centers. It was predicted that this would cause a strong dependence of HHG on molecular orientation [22] and the appearance of a diffraction pattern in ATI electrons emerging from elastic rescattering with the molecular ion [23,24]. These predictions are yet to be tested directly, but indirect evidence was found in Ref. [25].

From the work of Muth-Böhm *et al.* [16,17] emerged the idea that antisymmetric orbitals would contribute with opposite signs to the total ionization amplitude. However, if orbital symmetry is to play a defining role, then it is clear that the ionization probability should have a strong dependence upon the molecular orientation with respect to the electric field. The first theoretical study that included angular dependences was by Plummer and McCann [26], who investigated H₂⁺. Additionally, two-dimensional (2D) and 3D integration of the Schrödinger equation of the H₂⁺ molecular ion was performed to explore the harmonic generation efficiency as a function of the angle between the molecular axis and the laser polarization direction [27,28]. Very recently, Zhao *et al.* [29] have tackled this question anew, and with their molecular ADK method, they predict enhanced ionization of N₂ when it is aligned parallel to the electric field. In stark contrast, O₂ shows a local minimum in the ionization probability for the parallel configuration. The N₂ case has been given support recently by the experimental results of Corkum *et al.* [30], but there has been no equivalent experiment so far that studies O₂.

In this work we explore HHG in CO₂: a molecule whose highest-occupied molecular orbitals (HOMO) are antisymmetric. We approach the problem through both experiment

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and calculation. First, we solve the time-dependent Schrödinger equation in the single-active-electron approximation for a doubly antisymmetric initial wave function and look at both ionization and HHG for fixed orientations of the molecular axis with respect to the electric field. Second, we measure experimentally the HHG spectra of CO₂ for different preferential orientations of the molecular ensemble.

Most of the earlier experiments on ionization and HHG of molecules were performed in gas-phase isotropic ensembles of molecules. Experimental techniques that have only recently become common now allow us to work with ensembles of molecules that are preferentially aligned along a given direction in the laboratory frame [31,32]. This type of experiment has already provided us with partial insight into strong-field molecular processes [25,30,33,34], but this work is the first where the dependence of HHG on the orientation of the molecular axis is studied for a wide range of harmonics and for intermediate angles between parallel and perpendicular orientations.

To model the strong-field dynamics of the CO₂ molecule, we first note that the HOMO is doubly degenerate with π_g symmetry [35]. For arbitrary molecular orientations, we can choose the two degenerate orbitals such that the laser field is parallel to a nodal plane for one of the two. For this orbital, the recollision probability is small [19,20], so its contribution will be neglected. For the remaining HOMO orbital, the dynamics is simulated within a 2D single-active-electron model where the electron motion is restricted to the plane spanned by the laser field and the molecular axis. As effective binding potential we use a three-center soft-core potential of the form

$$V(\mathbf{r}) = -\frac{e^2 Z^C(r_c)}{\sqrt{r_c^2 + \varepsilon}} - \sum_{j=1,2} \frac{e^2 Z^O(r_{O,j})}{\sqrt{r_{O,j}^2 + \varepsilon}},$$

where the C and O labels refer to the carbon and oxygen atoms, respectively. We use the coordinates $\mathbf{r}_c = \mathbf{r}_e - \mathbf{R}_C$, $\mathbf{r}_{O,j} = \mathbf{r}_e - \mathbf{R}_{O,j}$ and screened nuclear charges $Z^O(r) = (Z_o^0 - Z_o^0)e^{-r^2/s^2} + Z_o^0$ for the oxygen cores and $Z^C(r) = (Z_i^c - Z_o^0)e^{-r^2/s^2} + Z_o^0$ for the carbon core. Here, \mathbf{r}_e , \mathbf{R}_C , $\mathbf{R}_{O,j}$ are the positions of the electron, the C core and the two O cores. The indices i and o denote the inner and outer limits of $Z^O(r)$ and $Z^C(r)$, i.e., the situation where the electron approaches the nucleus or infinity, respectively. We make the simple assumptions that the nuclei are always at least screened by the $1s$ electrons, and that for large excursions of the outer electron, a positive charge is left behind which is distributed equally over the three sites. This amounts to $Z_i^0 = 6$, $Z_i^c = 4$, $Z_o^c = Z_o^0 = 1/3$. The 2D equivalent of the π_g symmetry is a twofold mirror antisymmetry with a nodal line along the molecular axis and another nodal line in the perpendicular direction. We choose a softening parameter $\varepsilon = 0.5$ a.u., typical for 2D calculations, and adjust the screening parameter $s^2 = 0.623$ a.u. such that the IP of the lowest state with twofold antisymmetry matches the CO₂ value of 13.8 eV. The potential and the wave function are shown in Fig. 1. This orbital is taken as initial state for the numerical solution of the time-dependent Schrödinger equation by means of the split-operator method [36]. The wave function is represented on a rectangular grid with a typical size

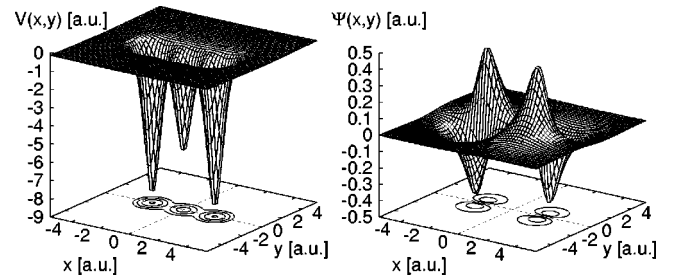


FIG. 1. Potential and initial wave function used for the numerical simulation of harmonic generation in CO₂.

of 490×120 a.u. We use pulses with a sine-squared field envelope and total length of 48 cycles. The spectrum of high harmonics is obtained by Fourier transforming the time-dependent dipole acceleration [37].

The results for 797 nm pulses of 2×10^{14} W/cm² intensity are shown on the left column of Fig. 2. The graphs illustrate the calculated orientation dependence of the harmonic intensities for the orders 9–17. In all cases, the intensity is low for parallel and perpendicular alignment and peaks at intermediate angles. This behavior is expected as a consequence of the twofold antisymmetry of the initial wave function, and, as will be shown below, is consistent with experiment. We have also confirmed that this behavior is

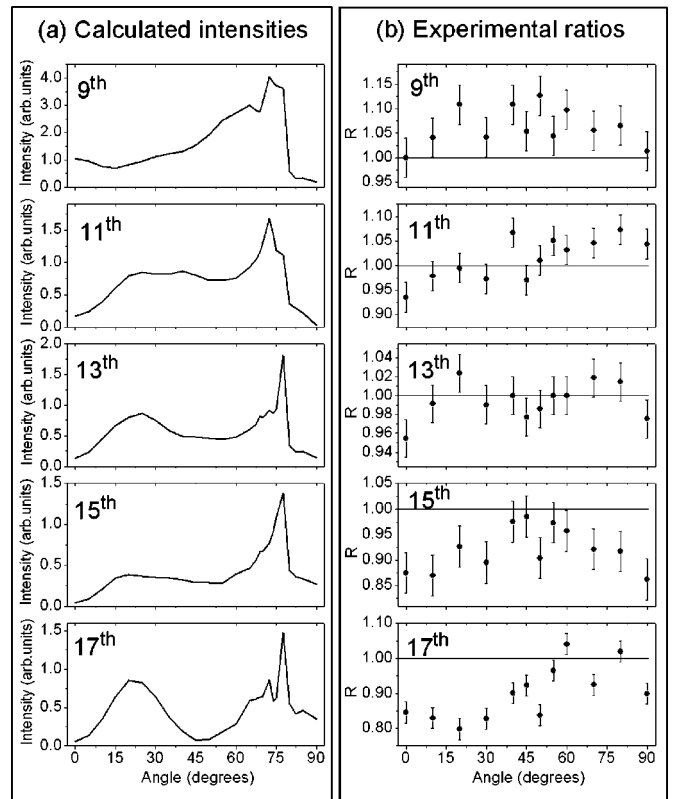


FIG. 2. (a) Calculated orientation dependence of the 9th to 17th harmonics for a laser with 797 nm wavelength and 2×10^{14} W/cm² intensity. (b) Experimental ratio of harmonic generation in CO₂ with and without the preparation beam present as a function of the relative polarizations of the preparation and the pump pulses in the range 0° – 90° .

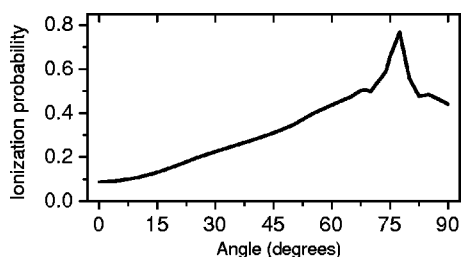


FIG. 3. Calculated orientation dependence of the ionization probability.

independent of the choice of the softening parameter.

For the orders 11–17, we observe a minimum in the range between 45° and 55° . Since this minimum does not move to larger angles of orientation as the harmonic order is increased, it is not clear whether it originates from a two-center interference effect as discussed in Refs. [21,22].

For all shown harmonics, the calculated intensity peaks sharply at about 75° . A corresponding peak is found in the orientation dependence of the ionization probability (Fig. 3), suggesting that this effect is due to resonant enhancement of ionization rather than recollision dynamics. Since resonances are very sensitive to the electronic level spacings, and therefore to the softening parameter, we do not expect full agreement between the experiment and the 2D results. Additionally, the calculations are done for the single molecule case, disregarding phase matching changes induced in the medium by an alignment laser beam, and therefore we will not tackle the question of the absolute changes in harmonic yield observed experimentally, but only its relative behavior for different angles.

The main conclusion of this analysis is that in a molecule with doubly antisymmetric orbitals, such as CO_2 , HHG should peak at intermediate angles. This is in contrast to HHG in the simpler systems H_2 and H_2^+ , where the ground-state orbitals are symmetric and calculations show that the harmonics exhibit maxima for parallel and perpendicular alignment [21].

Experimentally, in order to study how HHG depends on molecular orientation it is necessary to produce an aligned ensemble of molecules of sufficient density. Various methods may be used (see Ref. [38] for a recent review). In this paper we used the technique of adiabatic alignment with a strong off-resonant laser field [31,32]. The adiabaticity condition is always satisfied in our experiments, since the preparation pulse had a duration of 300 ps while the rotational period of CO_2 is 43 ps. The degree of alignment can be quantified using the expectation value of $\cos^2 \vartheta$ [39], where ϑ is the angle between the molecular axis and the electric-field vector. For an isotropic sample, $\langle \cos^2 \vartheta \rangle = 1/3$, whereas perfect alignment gives $\langle \cos^2 \vartheta \rangle = 1$. Using Ref. [39] with the estimated temperature of ~ 25 K in the jet [40], we estimate that the degree of alignment in the CO_2 ensemble was characterized by a value of $\langle \cos^2 \vartheta \rangle \approx 0.55$ for a preparation beam intensity of $2 \times 10^{12} \text{ W/cm}^2$. This moderate value limits our capacity to observe narrow features in the examination of angular dependences, but is high enough to observe the broad structures.

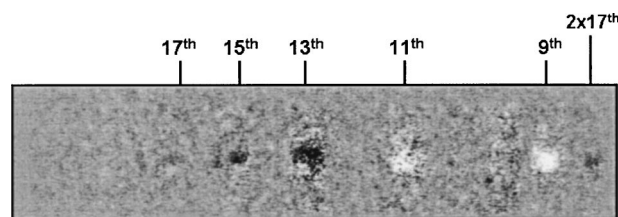


FIG. 4. Example of a “harmonic spectrum difference image” (see text). Lighter colors indicate enhancement of harmonic yield caused by the presence of the preparation pulse; darker colors indicate suppression.

This aligned ensemble of CO_2 molecules was studied as a source of HHG. The experimental setup is similar to that described in Ref. [25], but with the additional capability of having arbitrary polarization angles and spatial resolution at the detector end. We used a Ti:sapphire chirped pulse amplification laser system with a center wavelength of 797 nm and 60 mJ pulse energy. A beam splitter immediately before the grating compressor divided the laser pulse into two. The reflected beam was compressed to produce 70 fs full width at half maximum (FWHM) pump pulses. The transmitted fraction was left uncompressed to provide the 300 ps FWHM chirped preparation pulses. The pulses were recombined with a 50:50 beam splitter and copropagated through a 55 cm focal length lens into a vacuum chamber. A pulsed molecular jet was introduced into the interaction region, backed by a reservoir with CO_2 at pressures in the range 0.5–2.5 bar. In those conditions, formation of clusters is possible. Our own density-dependent HHG results show that this effect is negligible below 1.5 bar. Beyond that value, clustering increases gradually so that there are few monomers left at 5.5 bar [41]. The chamber was connected to a vacuum ultraviolet spectrometer equipped with an imaging microchannel plate detector. The phosphor screen was imaged onto a 12-bit charge-coupled device camera. Several harmonics were detected simultaneously, with spatial resolution in the vertical dimension. For each data point we recorded two (200-shot averaged) images, only in one of which the preparation beam was present.

Figure 4 shows the result of subtracting one of the harmonic spectra obtained with only the pump beam present from that obtained when the preparation beam, in this case with perpendicular polarization and $5 \times 10^{12} \text{ W/cm}^2$, was added. Typically, the preparation pulse produced changes of the order of 10–30 % in the HHG yield. We believe we can attribute this only moderate modulation, at least in part, to two effects: the relatively low degree of alignment, and HHG produced in clusters of CO_2 molecules [41], which are insensitive to alignment and therefore produce a constant background emission and partially mask the single molecule effects. For the chosen geometry, the harmonic generation region is situated around 3 mm before the center of the gas jet. At that point, the peak intensity of the pump beam is $7 \times 10^{14} \text{ W/cm}^2$, with a waist of $100 \mu\text{m}$, whereas the preparation beam, which attains a maximum intensity of $5 \times 10^{12} \text{ W/cm}^2$, has a waist of $24 \mu\text{m}$. Therefore, the effect of preparing the molecular sample was only visible in the central part of the harmonic. Figure 4 shows contrasting be-

havior for different harmonic orders. Under perpendicular polarization conditions, the 9th and 11th harmonics were enhanced, whereas the 7th, 13th, 15th, and 17th were suppressed. Under parallel polarization conditions, only the 9th harmonic was enhanced. The fact that HHG could suffer either enhancement or suppression as a consequence of alignment had been predicted by numerical models [25], but, to our knowledge, this is the first time that this effect is observed in an experiment.

For data analysis, the images with the HHG spectra when the preparation pulse was present were compared to those acquired when it was blocked. Vertical cross sections were taken across the emission region for each harmonic and the ratios of enhancement or suppression with respect to the isotropic ensemble were measured in the center of the emission profile. These are the ratios R shown in Fig. 2(b), where the change in harmonic yield was studied as the alignment angle was varied. For this experiment, keeping the preparation energy constant for all angles forced us to use the lower intensity value of 2×10^{12} W/cm², for which the contrast is significantly lower than at 5×10^{12} W/cm² but high enough to detect observable changes in the spectrum. Interestingly, not all harmonics showed identical behavior. The 11th harmonic suffers maximum change, the emission being suppressed when the ensemble is preferentially aligned parallel to the pump field, but enhanced when aligned perpendicular to it. The 17th harmonic shows similar features: while aligning the sample always results in suppression of the harmonic emission relative to the isotropic case, the situation where the molecular axis is preferentially aligned perpendicularly to the perpendicular case is by far more favorable than parallel. Emission of those harmonics seems to follow the calculated ionization probability curve shown in Fig. 3. For the 9th,

13th, and 15th harmonics, the emission peaks for intermediate angles, and the general structure confirms what was found numerically, that is, local minima at 0° and 90°, as would be expected for symmetry reasons. However, the errors associated with the measurement and the limited degree of alignment do not allow us to confirm or discard the existence of detailed structure for intermediate angles such as was shown in Fig. 2(a). Equally, we cannot confirm the presence of the interference effect in recollision [21,22]. Further experimental work is required to clarify this point.

The observation of a reduced HHG yield when the molecular axis is parallel to the electric field, relative to other orientations—a feature that is common to all high harmonics observed—is contrary to what has been found recently in N₂ [42]. This supports the idea that it is the antisymmetric nature of the HOMO orbitals in CO₂ that causes harmonic yield to maximize at angles other than 0°.

In summary, qualitative agreement has been found between the calculated HHG in a system characterized by an antisymmetric wave function and the observed orientation dependence of HHG in CO₂. The work offers evidence that the symmetry of the molecular ground state gets imprinted in the outcome of strong-field phenomena. We believe this can allow us to exert further control on HHG itself, a process that is experiencing renewed interest as a source of attosecond pulses.

We gratefully acknowledge useful discussions with O. Rubner, V. Herrero, J. W. G. Tisch, K. J. Mendham, and E. Sali and the technical assistance of P. Ruthven and A. Gregory. The work was supported by the EPSRC, the EU “CO-COMO” network, and the British-Spanish *Acciones Integradas* Scheme.

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