Direct Measurement of the Angular Dependence of Ionization for N_2, O_2, and CO_2 in Intense Laser Fields

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We experimentally measure the ionization probability as a function of alignment angle of three molecules in intense laser fields: nitrogen, oxygen, and carbon dioxide. Unlike atoms, molecules have a rotational degree of freedom. By controlling the alignment of the molecule relative to the laser field, molecules offer additional ways to understand strong-field ionization. The angular dependence of ionization directly maps to the orbital symmetry of each molecule. Carbon dioxide is seen to have a very sharp preference for ionization when aligned at 45 degrees to the laser field, in significant disagreement with current theories.

PACS numbers: 33.80.Rv, 42.50.Hz

Ionization of molecules in intense laser fields is a fundamental process that underlies most molecular strong-field phenomena such as high-harmonic generation [1,2], above-threshold ionization, laser-induced electron diffraction [3], and double ionization. In the past few years, molecular electrons have found important applications in imaging of molecular orbitals [4] and probing nuclear dynamics with attosecond resolution [5]. Therefore, it is not surprising that understanding molecular ionization has become an important goal.

For all of the above mentioned processes, it is particularly important to know the angular dependence of the ionization probability. From a fundamental physics perspective, the rotational degree of freedom offered by molecules gives another handle, the orientation of the molecule, that can shed light on the role of the shape and symmetry of the molecular orbitals that contribute to the ionization process.

We report direct measurements of the angular dependence of ionization for N_2, O_2, and CO_2. Briefly, we align rotationally cold gas phase molecules with a pump pulse, and record ionization yield from a probe pulse as a function of the angle between the polarization axes of the two pulses. We find surprisingly different angular dependencies for O_2 and CO_2, which both have highest occupied molecular orbitals (HOMO) with the same π_g symmetry. The results suggest a much stronger destructive interference in CO_2 that challenges current theoretical models.

Theoretically, exact ionization rates from the time-dependent Schrödinger equation can be calculated only for the one-electron H_2^+ molecule [6]. For multielectron systems, the development of ionization models was motivated by the finding that, for many molecules, ionization is suppressed compared to atoms of a similar ionization potential [7,8]. By extending the many body S-matrix theory to molecules, Muth-Böhm *et al.* predicted that ionization suppression should occur in homonuclear diatomic molecules with antisymmetric HOMOs due to a destructive interference of electrons emitted from the two centers [9,10]. Alternatively, Tong *et al.* [11] have developed a tunneling molecular ADK model (MO-ADK) as an extension of the corresponding atomic theory. Both models have been only partially successful in explaining the ionization suppression, while their predictions on angular dependence of ionization has not been thoroughly tested experimentally.

Litvinyuk *et al.* [12] measured the ionization yield of N_2 for two molecular alignment distributions and found that ionization is about 4 times more likely for molecules aligned parallel to the laser field than for molecules perpendicular to it. Pinkham and Jones [13] determined the ratio for CO. Recently, Alnaser *et al.* [14] measured the angular distribution of fragments produced in dissociative double ionization of several molecules. However, the process involved several steps (ionization, electron recollision, collisional excitation, and dissociative ionization), which can all contribute to the measured angular distribution, and so the interpretation of the results is not straightforward.

In order to measure the angular dependence of ionization, it is essential to create an ensemble of highly aligned field-free molecules. We used a Ti:sapphire laser system (800 μJ, 40 fs, 820 nm, 600 Hz), and split the pulse into an aligning pulse and a probe pulse with an adjustable delay. The two beams were recombined and focused by a $f = 50$ mm parabolic mirror into the sample gas. The purpose of the aligning pulse is to create a coherent superposition of rotational states, i.e., a rotational wave packet, which at revival times exhibits macroscopic field-free alignment around the polarization axis of the aligning pulse [15]. In the case of N_2, O_2, and CO_2 we used the first full (8.5 ps), the first quarter- (3.0 ps), and the first half-revival (21.0 ps), respectively.

A gas mixture consisting of the sample molecule, a reference noble-gas atom with a similar saturation intensity (Ar or Kr), and a buffer gas, was expanded into the vacuum chamber through a 75-μm nozzle at a stagnation pressure

of about 200 Torr. The buffer gas of helium or argon provided rotational cooling of the sample molecules. The measured translational temperature for the three different gas mixtures was 9–31 K. The degree of alignment was optimized by stretching the aligning pulse with different amounts of SF6 glass to about 70–300 fs.

Before measuring the ionization rates, we first measured the degree of alignment of the molecular ensemble. The orientation of each molecule was detected by Coulomb explosion in a time-of-flight mass spectrometer [16]. The probe pulse was an intense ($\sim 10^{16}$ W/cm^2) circularly polarized pulse. All three velocity components of each ion were determined from the time and position sensitive detector. From that we found the alignment angle ϑ, defined as the angle between the polarization axis of the aligning beam and the velocity component projected onto the plane of the exploding pulse [16]. For a diatomic molecule X_2, we took the velocity of one of the correlated fragments from the $X_2 \rightarrow X^{2+} + X^{3+}$ channel. In the case of CO_2, in order to reduce the effect of the bending vibrational motion, we took the vector difference between the velocities of correlated O^{2+} and O^{3+} fragments. The measured alignment distribution, $A(\vartheta)$, is shown in Fig. 1 for CO_2.

We then measured the angular dependence of ionization by recording the ion yield as a function of the angle α between the polarization axis of the ionizing field and the main axis of the alignment distribution. The probe pulse was horizontally polarized, and the polarization axis of the aligning pulse was rotated with a combination of a half- and a quarter-wave plate. To minimize the effect of intensity fluctuations, we took the ratio of the simultaneously measured single-ionization yields of molecules and the companion reference atoms (N_2^+/Ar^+, O_2^+/Kr^+, CO_2^+/Kr^+). In all three cases, only the single charged molecular and atomic ions were observed.

Figure 2 shows the measured relative ionization yields, $M(\alpha)$, for N_2, O_2, and CO_2. The angular dependencies of ionization for the three molecules are clearly different, reflecting the symmetry of the HOMO (σ_g for N_2, and π_g for O_2 and CO_2). Generally, the highest contrast in the angular dependence was observed at the lowest intensities.
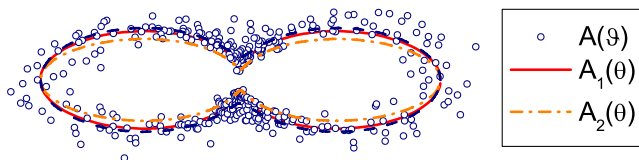

FIG. 1 (color online). Alignment distribution of CO_2 molecules with respect to the polarization axis of the aligning beam (horizontal). The dots are the measured angular distribution $A(\vartheta)$ calculated from the vector difference between the velocities of the correlated pairs of O^{2+} and O^{3+} fragments. The dashed line is the best fit to $A(\vartheta) = 1 + a/\sqrt{\cos^2 \vartheta + \epsilon^2 \sin^2 \vartheta}$. The two limiting cases of the actual alignment distribution, $A_1(\theta)$ (no realignment) and $A_2(\theta)$ (complete realignment into the polarization plane), are also shown.

We seek $S(\theta)$, the angle-dependent ionization probability, where θ is the angle between the polarization axis of the ionizing field and the internuclear axis. The measured ionization signal $M(\alpha)$ is the convolution of $S(\theta)$ with the alignment distribution

$$M(\alpha) = C \int_{\phi'=0}^{2\pi} \int_{\theta'=0}^{\pi} S[\theta(\theta', \phi'; \alpha)] A(\theta', \phi')$$
$$\times \sin(\theta') d\theta' d\phi'. \qquad (1)$$

Here θ' and ϕ' are the polar and azimuthal angle in the frame about the polarization axis of the aligning beam, $A(\theta', \phi')$ is the alignment distribution per steradian in that frame, and C is a constant. For linear molecules, the ionization rate $S(\theta)$ depends only on the angle θ, which is given by

$$\cos\theta = \cos\alpha \cos\theta' - \sin\alpha \sin\theta' \sin\phi'. \qquad (2)$$

Before deconvolving Eq. (1), we will first discuss the relationship between $A(\theta, \phi)$ and the measured distribution $A(\vartheta)$. The circularly polarized pulse that was used to probe the angular distribution had no bias in the explosion of molecules that lay within its plane of polarization. For a molecule lying outside of this plane, it is possible that the intense laser field could apply a torque to the molecule that could cause it to partially align into the plane as it explodes. Thus it is not possible to unequivocally determine the degree of alignment outside of the plane of polarization of the probe pulse. We assume that $A(\theta, \phi)$ is cylindrically symmetric around the polarization axis of the aligning beam, i.e., $A(\theta, \phi) = A(\theta)/2\pi$. Since the Coulomb explosion technique measures the projected angle ϑ, the distributions $A(\vartheta)$ and $A(\theta)$ are generally not the same.

We explore the two limiting cases, based on the degree to which the intense Coulomb explosion pulse perturbs the out-of-plane distribution. (i) No realignment of the molecules takes place. The out-of-plane ionization rate may be lower. Because of the relatively small measured out-of-plane width of the distribution (FWHM of about 20°), the actual distribution $A_1(\theta)$ will be close to the measured distribution $A(\vartheta)$. (ii) The molecules have been completely realigned into the plane of the circularly polarized pulse. The actual distribution $A_2(\theta)$ will be narrower than the measured distribution $A(\vartheta)$.

In Fig. 1, we show the distributions $A_1(\theta)$ and $A_2(\theta)$ as calculated with the above assumptions from the measured distribution $A(\vartheta)$. It can be seen that the underlying distributions A_1 and A_2 are not very different from the measured distribution.

Now that we have measured the ionization yield $M(\alpha)$ and the alignment distribution $A(\theta, \phi)$, we can proceed to reconstruct the angular dependence of ionization, $S(\theta)$. We assume a functional form of $S(\theta)$, and then fit $M(\alpha)$ using Eq. (1) to the data in Fig. 2. We first write $S(\theta)$ as a linear combination of Legendre polynomials, $S(\theta) = \sum_{i=0}^{3} a_{2i} P_{2i}(\cos\theta)$, to show the underlying symmetry. A
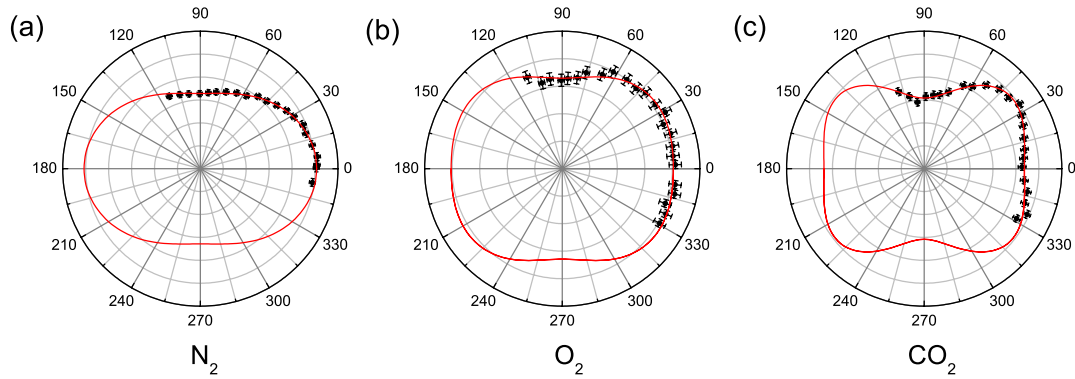
FIG. 2 (color online). Measured ionization yield $M(\alpha)$ as a function of the angle α between the polarization axes of the aligning and the ionizing beams for (a) N_2, (b) O_2, and (c) CO_2. The error bars in the ionization yields are estimated from the results of different experimental runs. The solid lines are the best fits using the corresponding functional forms shown in Fig. 3. The peak laser intensities and the degrees of alignment, $\langle \cos^2 \vartheta \rangle$, are, respectively: (a) 1.5×10^{14} W/cm^2, 0.77; (b) 1.3×10^{14} W/cm^2, 0.78; (c) 1.1×10^{14} W/cm^2, 0.73.

very good fit was achieved with this expansion in the cases of N_2.

For O_2 and CO_2, the best-fit results yielded a butterfly-like distribution, as expected from the π_g symmetry of the HOMO. Based on this confirmation of symmetry, a more specialized basis set was found to improve the least-squares error, namely, $S_{\pi_g}(\theta) = \cos^n(\theta - \theta_m) + \cos^n(\theta + \theta_m)$.

The best-fit ionization signals $S(\theta)$ are shown in Fig. 3 for the two limiting cases of alignment. The deconvolved alignment distributions are much sharper, particularly in the case of CO_2 for which the molecular alignment distribution was broader. We found that the two-parameter fit on the function $S_{\pi_g}(\theta)$ is stable and that the small changes in the fitting curve does not change the deconvolved distributions in Fig. 3 significantly. In Fig. 3 we also show the predictions of the MO-ADK model [11]. Following the procedure in Tong *et al.* [11], we first calculate ionization rates as a function of the angle θ and laser intensity. This

rate is averaged over a 45-fs (FWHM) pulse and a Gaussian beam distribution with a waist diameter of 10 μm and the measured peak laser intensity.

For N_2, the angular dependence $S(\theta)$ in Fig. 3(a) is less peaked than the one predicted by MO-ADK. We find that, at 1.5×10^{14} W/cm^2, ionization is 3.3 ± 0.4 times higher for the parallel alignment ($\theta = 0°$) than for the perpendicular alignment ($\theta = 90°$) if no realignment is assumed, and 2.3 ± 0.3 if complete realignment is assumed. Molecular ADK predicts the parallel vs perpendicular ratio to be about 10:1 at 1.5×10^{14} W/cm^2 (Fig. 3), and about 6.5:1 at 3.0×10^{14} W/cm^2. The disagreement with the model observed in this work is larger than reported in in Litvinyuk *et al.* [12], 4.5 ± 0.5, but that work was done at a slightly higher intensity and without averaging over the focal volume.

The MO-ADK predictions for O_2 are in relatively good agreement with our measurements. The main difference is that the measured maximum at about 45° deviates from the
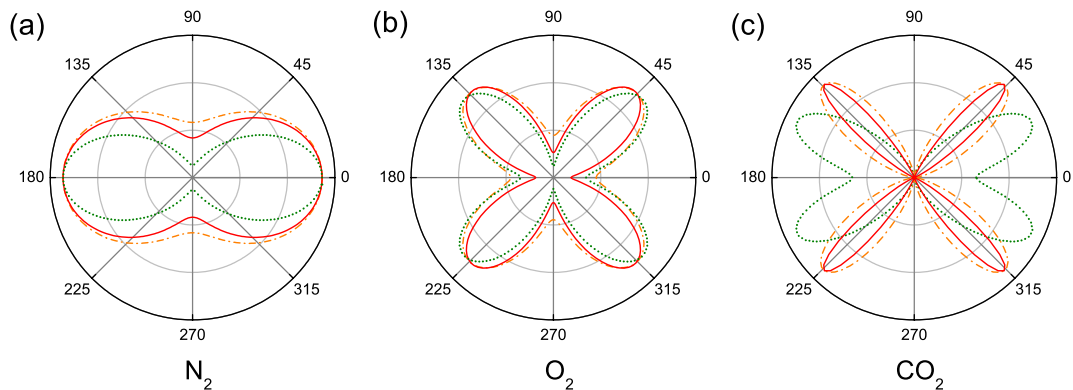

FIG. 3 (color online). Angular dependence of the ionization signal $S(\theta)$ after deconvolution with the alignment distribution: (a) N_2, (b) O_2, and (c) CO_2. The curves are the result of the best fit of Eq. (1) to the measured yields in Fig. 2 using parameterized $S(\theta)$ (see text). The results are shown for the two limiting cases of the alignment distribution (as shown in Fig. 1 for CO_2): $A_1(\theta)$, no realignment (solid line), and $A_2(\theta)$, complete realignment (dash-dotted line). The dotted line is the ionization signal calculated with the molecular ADK model and the experimental intensity distribution.

predicted maximum at 40°. In the case of CO_2, the angular dependence is remarkably peaked with very little ionization at 0° and 90°. We find that ionization is maximum at about 46°, whereas the MO-ADK model predicts 25°.

The most remarkable result of our experiment is the narrowness of $S(\theta)$ for CO_2. We have eliminated possible experimental causes of this apparent narrowness. For example, in order to make the lobes of $S(\theta)$ for CO_2 to be as broad as for O_2, we would require an alignment distribution with $\langle \cos^2\theta \rangle = 0.87$, and even then they would still peak at 46°. Such a high degree of alignment is not possible with the rotational temperature of our molecular beam, given the measured translational beam temperature of 10 K. There may also be some weak realignment due to the probe pulse [17], but this would reduce the sharpness of the lobes. The possible effect of vibrational bending on the measured angular dependence of ionization would also go in the same direction.

We now focus on why the measured CO_2 ionization is markedly different from MO-ADK calculations. The Keldysh parameter is 1, so the ionization process is not in the pure tunnel ionization regime which MO-ADK theory assumes, hence multiphoton effects may play a role.

The suppression of the ionization probability along 0° and 90° is a direct manifestation of the destructive interference predicted in [9]. Such destructive interference is not well described within the MO-ADK model. S-matrix theory [10] does include interference and multiphoton effects, yet it too does not predict as narrow a distribution as we observe [18]. Such interference effects could also explain recent reports of much lower high-harmonic signal in CO_2 compared to Kr, whereas no such suppression was observed in case of O_2 and Xe [19]. We note that a similarly narrow angular dependence of ionization as in Fig. 3(c) was also found in *ab initio* calculations for an excited state π_g orbital of H_2^+ [6], although at much lower intensity and longer wavelength.

The differences observed between O_2 and CO_2, both with a π_g HOMO, might be due to multielectron effects that are not properly taken into account in any single-active electron model. For example, Hartree-Fock calculations for CO_2 show that the electron density of all inner orbitals together has a minimum around 45°. The smaller exchange interaction of the ionizing electron with other electrons could confine ionization within a narrower range of angles. Also, the smaller energy separation among the valence orbitals of CO_2 is known to result in a higher polarizability. The remaining electrons may collectively push out the detached electron through polarization of the core [20]. Finally, multiphoton excitation and ionization through an excited (including Rydberg) state could also lead to a different angular dependence of ionization.

In conclusion, we have made experimental measurements of the angle dependence of ionization rate for three molecules in intense laser fields. Both N_2 and O_2 were in reasonable agreement with current theories of tunnel ionization from molecules. However, the ionization of CO_2 was surprisingly sharp at 45°, in disagreement with model predictions. Ionization of molecules in intense laser fields is a complex problem that will probably require a proper treatment of many-electron effects in future models.

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