## Signatures of symmetry-induced quantum-interference effects observed in above-threshold-ionization spectra of molecules

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We report on an experimental observation of the qualitative signatures of symmetry-induced quantuminterference effects in above-threshold-ionization spectra of O<sub>2</sub> (antibonding  $\pi_g$  symmetry) and N<sub>2</sub> (bonding  $\sigma_g$  symmetry). It confirms the corresponding predictions of intense-field S-matrix theory.

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For intense femtosecond laser pulses, the probability of ionization of a diatomic or a polyatomic molecule is found to be lower than, or at best equal to, that of an atom with a comparable ionization potential (called a "companion" atom). This so-called "suppressed" ionization of molecules, in fact, has been observed in a wide range of diatomic and polyatomic molecular systems (Chin and co-workers [1], Gibson and co-workers [2], Corkum and co-workers [3]). Furthermore, most, if not all, of the more complex organic molecules studied so far have been found to be harder to ionize in intense laser pulses than their atomic companions. Besides its intrinsic interest in nonperturbative quantum physics, an understanding of this unexpected behavior is of interest, e.g., for photochemical reactions, for laser-plasma physics, for efficient high harmonics generation, or for the study of the propagation of intense short laser pulses in the atmosphere [4].

An interpretation of the ionization reduction phenomenon in molecules has been proposed recently (Faisal and coworkers [5,6]) where it has been shown explicitly by a lowest-order S-matrix analysis that the antibonding symmetry of, e.g.,  $O_2$  introduces a reduction of the ionization yield of the molecule by a destructive interference of the two subwaves of the ionizing electron emerging from the two atomic centers, but not, e.g., for N<sub>2</sub>, which has a bonding symmetry [7]. These results are also found to agree with the available experimental data [1,2] of ionization yields of these molecules as well as of their "companion" atoms, Xe and Ar. It is interesting to compare this influence of symmetry of the valence orbital with the role of vibrational motion. Although the latter motion causes some reduction in the case of H<sub>2</sub> and O<sub>2</sub>, it was found to be too small to account for the experimental results [8]. Another proposal [9] invokes possible multielectron effects and uses a heuristic fixed one-electron model to define an effective charge. This is used in a tunneling formula [10] to estimate the yields of  $O_2$  and Xe that show the desired reduction for  $O_2$ . However, the yields themselves differ widely from the observations except in the saturation domain.

The influence of the symmetry-induced quantuminterference dynamics on the intense field ionization of diatomic molecules should leave its footprint at a deeper level than that offered by the total ionization yields. This can therefore provide an independent test of any theory of intense-field molecular ionization process. Thus, the purpose of this Rapid Communication is twofold: to analyze the qualitative signatures of the symmetry-induced interference effect on the above-threshold ionization (ATI) spectra of diatomic molecules of antibonding or bonding symmetry, *and* to report an experimental observation of the same in the ATI spectra of the diatomics O<sub>2</sub> (antibonding  $\pi_g$  symmetry) and N<sub>2</sub> (bonding  $\sigma_g$  symmetry).

The active molecular orbitals of homonuclear diatomic molecules, expressed in the convenient linear combination of atomic orbitals (-molecular orbitals) representation [11], are of the form (atomic units,  $e=\hbar=m=1$ , are used throughout)

$$\Phi(\mathbf{r};\mathbf{R}_1,\mathbf{R}_2) = \sum_{i=1}^{i_{max}} a_i \phi_i(\mathbf{r},-\mathbf{R}/2) + b_i \phi_i(\mathbf{r},\mathbf{R}/2). \quad (1)$$

Here, the atomic orbitals  $\phi_i$  are centered at  $\mathbf{R}_1 = -\mathbf{R}/2$  and  $\mathbf{R}_2 = \mathbf{R}/2$ , where *R* is the internuclear separation. For a bonding molecular orbital ( $\sigma_g$  or  $\pi_u$ ), both sets of coefficients  $a_i$  and  $b_i$  have the same value and sign, i.e.,  $a_i = b_i$ , while, in contrast, for an antibonding orbital ( $\sigma_u$  or  $\pi_g$ ), they have the opposite sign, i.e.,  $a_i = -b_i$ . The above-threshold-ionization spectra of present interest can be obtained theoretically [5,6,12,13] from the leading term of the so-called intense-field many-body *S*-matrix theory [12,14]. This term is analogous to the so-called Keldysh-Faisal-Reiss model [15], and can be written down as [16]

$$\Gamma_{N}^{+} = \int d\hat{\mathbf{k}}_{N} \left( \frac{dW^{(N)}}{d\hat{\mathbf{k}}_{N}} \right)_{at} \\ \times \begin{cases} \sin^{2}(\mathbf{k}_{N} \cdot \mathbf{R}/2), & \text{antibonding} \\ \cos^{2}(\mathbf{k}_{N} \cdot \mathbf{R}/2), & \text{bonding,} \end{cases}$$
(2)

where

$$\left(\frac{\mathrm{d}W^{(N)}}{\mathrm{d}\mathbf{\hat{k}}_{N}}\right)_{at} = N_{e} 2 \pi C_{Coul} k_{N} (U_{p} - N\omega)^{2}$$
$$\times J_{N}^{2} \left(\boldsymbol{\alpha}_{0} \cdot \mathbf{k}_{N}, \frac{U_{p}}{2\omega}\right) \left|\sum_{i=1}^{i_{max}} 2a_{i} \langle \mathbf{k}_{N} | \boldsymbol{\phi}_{i} \rangle\right|^{2}, \quad (3)$$

 $N_e$  is the number of electrons in the active molecular orbital and  $C_{Coul} = (2 \kappa_{ion} E_{ion} / E_0)^{2Z/\kappa_{ion}}$  is a correction factor that accounts for the final-state Coulomb interaction of the Volkov electron with the residual ion [17,18], where Z is the charge state of the molecular ion (Z=1 for single ionization) and  $E_0$  is the peak field strength of the laser.  $J_n(a;b)$  is a generalized Bessel function of two arguments that arises from the Fourier decomposition of the Volkov wave function (e.g., [19]).  $k_N^2/2 = N\omega - (U_p + E_{ion})$  is the kinetic energy of an electron on absorption of N photons,  $U_p = I/4\omega^2$  is the so-called ponderomotive (or quiver) energy of an electron in the laser field of frequency  $\omega$  and intensity I, and  $E_{ion}$  $\equiv \kappa_{ion}^2/2$  is the ionization energy of the molecule.

The *N*-photon ionization rates  $\Gamma_N^+$  for all allowed *N*s such that  $N\omega \ge E_{ion} + U_p$ , define the ATI spectra of the two classes of diatomic molecules having active molecular orbitals of the bonding or the antibonding symmetry. The destructive and constructive interference effects in the ionization rates manifest themselves in the sine squared and the cosine squared terms of Eq. (2). We may now inquire as to what are the qualitatively significant effects of the symmetry of the molecular wave function on the ATI spectra. Equation (2) suggests that for a diatomic molecule with antibonding valence orbital, the destructive interference will be effective for small values of  $\mathbf{k}_N \cdot \mathbf{R}/2$  that correspond to the lowest few peaks of the ATI spectrum for which the electron momenta  $k_N$  are small. Furthermore, from the behavior of the sine squared function, one also expects that the effect of the destructive interference would decrease gradually with the increase of its argument. In contrast, in the case of bonding symmetry, in the same region of energy, the cosine squared term would be comparable to unity, and hence there should be no significant reduction of the ATI peaks. Thus the lowest-order S-matrix theory predicts the following qualitative signatures of the interference effect on the ATI spectra of the  $\mathrm{O}_2$  (antibonding  $\pi_g$  symmetry) and  $\mathrm{N}_2$  (bonding  $\sigma_g$ symmetry) molecules: (i) the lowest energy ATI peaks of  $O_2$ should be reduced significantly compared to that of its companion atom Xe; (ii) the peaks in the ATI spectra of O<sub>2</sub> would approach from below that of Xe with increasing energy until the interference effect becomes ineffective for high energy; and (iii) the ATI peaks of N<sub>2</sub> will not exhibit the signatures (i) and (ii), but rather should be comparable to that of its companion atom Ar. We may add that these effects are

10<sup>-1</sup> 10 O. 10<sup>-1</sup> ⊃—o Xe 10<sup>-2</sup> 10<sup>-3</sup> ₩ 10<sup>-6</sup> (b) 10<sup>-6</sup> 10 20 0 10 0 10 25 15 20 25 5 15 5 30 electron energy [eV] electron energy [eV]

FIG. 1. Calculated ATI spectrum of O<sub>2</sub> (filled circles) and that of its companion atom Xe (open squares) at  $\lambda = 800$  nm and two intensities, panel (a)  $I = 10^{14}$  W/cm<sup>2</sup>, and panel (b) I = 2 $\times 10^{14}$  W/cm<sup>2</sup>. Note (i) the "suppression" of the ATI peaks of O<sub>2</sub> at low energies, and (ii) their approach toward the spectrum of Xe with increasing energy.



FIG. 2. Same as Fig. 1, but for  $N_2$  (filled circles) and Ar (open squares). Note the similarity of the molecular and atomic spectra in this case.

purely quantum mechanical in nature and cannot be explained by classical arguments, unlike some properties of ATI spectra of atoms.

To check the above theoretical expectations, we have first performed calculations of the above-threshold-ionization spectra of  $O_2$  and  $N_2$ , using Eq. (3), along the polarization axis for an intense Ti:sapphire laser pulse of  $\lambda = 800$  nm. The corresponding calculations for the ATI spectra of the companion atoms, Xe and Ar, are also carried out for comparison. The ground-state wave functions for the molecules were obtained from the respective Hartree-Fock methods with default Gaussian basis sets extended by an additional diffuse s and a p function, using the GAMESS code [20]. The calculated rates for the molecules were orientation averaged, assuming random orientations of the molecular axis with respect to the laser polarization axis [21]. The basic rates were used in the rate equations to obtain the final ATI yields to be compared with the experiment (see below), by integrating over the Gaussian pulse profile and summing over the contributions from all points of a Gaussian focal distribution (TEM<sub>00</sub>) mode). The pulse durations and the focal parameters are chosen to be as that of the experiment.

Figure 1 shows the calculated spectra of  $O_2$  (filled circles) and those of Xe (open squares), for the ejection of the electrons along the polarization axis of the linearly polarized field, at two different peak intensities, (a)  $I=10^{14}$  W/cm<sup>2</sup> and (b)  $I=2\times10^{14}$  W/cm<sup>2</sup>. It can be seen from the figure that the calculated spectra clearly exhibit both the signatures (i) and (ii); i.e., the "suppression" of the lowest-energy ATI peaks of  $O_2$  compared to that of Xe, and the approach of these peaks to those of the Xe with increasing energy, until



FIG. 3. Experimental ATI spectra of  $O_2$  (gray) and Xe (black) at peak intensities of approximately (a)  $10^{14}$  W/cm<sup>2</sup> and (b) 2  $\times 10^{14}$  W/cm<sup>2</sup>. While the absolute value of the intensity has an error of 10–20%, the error of their ratio is negligible. The wavelength was 800 nm and the pulse duration 50 fs. For both species the experiment was operated with the same background pressure within approximately 10%.



FIG. 4. Same as Fig. 3, but for  $N_2$  (gray) and Ar (black).

the energy becomes too high for the destructive interference to be effective. In Fig. 2 we show the corresponding results of calculations for  $N_2$  (filled circles) and Ar (open squares). As expected for this symmetry, both the signatures (i) and (ii) are now *absent*, and indeed, in accordance with (iii), the  $N_2$  spectrum is seen to remain comparable to that of its companion Ar atom. We note parenthetically that the small modulations, observed here for the molecular ATI spectra, are reminiscent of another quantum effect that was first observed in the atomic case [23] and have been explained as due to the interference of quantum trajectories of the photoelectron [23,24] that appear when the so-called classical simple man's model of ionization is reinterpreted in the spirit of Feynman's path integrals [24,25].

To test the existence or otherwise of the qualitative signatures of the symmetry-induced interference effects on the ATI spectra of diatomic molecules, we have performed experiments to measure the spectra of O<sub>2</sub> (antibonding symmetry) and  $N_2$  (bonding symmetry), as well as those of their companion atoms Xe and Ar. We have used a Ti:sapphire laser system that consists of a 20-fs oscillator, a cw-pumped amplifier, and a large prism compressor. It produces pulses with standard properties (e.g., intensities in excess of  $10^{14}$  W/cm<sup>2</sup>), but with an extremely high repetition rate of 100 kHz. The photoelectrons are recorded with a time-offlight spectrometer. Fast timing electronics, together with specifically written data acquisition software, made it possible to handle electron count rates of 200 kHz and more. The laser polarization axis was oriented parallel to the axis of the photoelectron spectrometer. Great care was taken in order to maintain the same pressure and the same number of shots for both the molecular and the atomic gases.

Figure 3 shows the ATI spectra of  $O_2$  and Xe at two peak intensities  $I = 10^{14}$  W/cm<sup>2</sup> and  $2 \times 10^{14}$  W/cm<sup>2</sup>. It can be seen from the figure that the lowest-energy ATI peaks for  $O_2$ are suppressed compared to those of Xe and in conformity with the qualitative prediction (i) above. Also the difference between the spectrum of  $O_2$  and Xe tends to decrease with increasing electron energy as expected in (ii) above. In Fig. 4 we compare the measured ATI spectrum of  $N_2$  and that of its companion atom, Ar, for the same laser parameters. It can be seen from the figure, that unlike in the antibonding case of  $O_2$  (Fig. 3), the ATI spectrum of  $N_2$  does not show suppressed peaks at the lowest energies, but in fact remain comparable to that of its companion atom Ar, as expected for the bonding case, signature (iii) above.

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FIG. 5. Experimental ATI spectra of  $O_2$  (gray) and Xe (black) at  $10^{14}$  W/cm<sup>2</sup>, extended to high energies. Note the absence of the plateau in  $O_2$ , while it is well developed in Xe.

Finally, we have also measured the yields at higher electron energies where the interference effect becomes ineffective. This reveals a further effect of destructive interference that is not discussed above within the present lowest-order S-matrix analysis. To understand this qualitatively, we first recall the well-known fact that in the atomic case an ATI spectrum can exhibit a plateau at high energies [26]. Its origin is due to the "boosting" of the initially released lowenergy electrons to high energies by *rescattering* off the ion core. As expected, we observe in Fig. 5 a high-energy rescattering "plateau," which is well developed for Xe, but it is very weak, if present at all, for  $O_2$ . What is the origin of this anomaly, which we observe here, in the case of O<sub>2</sub>? Within the rescattering scenario this could be understood as a consequence of the same symmetry-induced destructive interference effect that suppresses the ionization probability of the low-energy electrons. This causes a much reduced number of electrons to start with, which cannot add up to the height required for a well developed plateau when boosted to high energies by rescattering. It would be of interest to investigate this effect more quantitatively in the future.

To conclude, the *S*-matrix theory of intense-field molecular ionization predicts that the above-threshold-ionization (or ATI) spectrum of  $O_2$  would be suppressed compared to that of its "companion" atom (Xe), due to a quantum destructive interference effect induced by the antibonding symmetry character of its active molecular orbital. In contrast, the ATI spectrum of N<sub>2</sub>, which has a bonding symmetry, is expected to remain comparable to the ATI spectrum of its companion atom (Ar). Experimental observations are reported here that confirm the theoretical predictions discussed above.

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