

## Suppressed Molecular Ionization for a Class of Diatomics in Intense Femtosecond Laser Fields

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It is shown that the puzzling experimental observation of suppressed molecular ionization, in intense laser fields, of  $O_2$ , and its absence in  $N_2$ , is a symmetry induced dynamical effect. More generally, it is predicted that the ionization signal of the class of homonuclear diatomic molecules having valence orbitals with an antibonding symmetry (e.g.,  $\sigma_u$ ,  $\pi_g$ ) would be suppressed, but not those with a bonding symmetry (e.g.,  $\sigma_g$ ,  $\pi_u$ ). The suppression effect can be visualized as due to an effective destructive interference between the two subwaves of the ionizing electron emerging from the two atomic centers.

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Recently, nonlinear phenomena associated with ionization of molecules in intense laser fields have generated considerable experimental and theoretical interest (e.g., [1]). Earlier, it had been found experimentally [2–4] that in intense laser fields ionization signals of molecules and noble gas atoms with comparable ionization energies behaved similarly. This was often assumed to be understood in terms of a tunneling ionization process in which the probability of ionization depends primarily on the ionization energy of the system (e.g., [5]). Thus, for example, the ionization signals of the pair  $N_2$  and Ar with analogous ionization energies [ $E_{\text{ion}}(\text{Ar})/E_{\text{ion}}(\text{N}_2) = 15.76 \text{ eV}/15.58 \text{ eV} = 1.01$ ] showed very similar results as a function of intensity [2,4]. Recently, however, a strong deviation from this general expectation is discovered in two independent experiments using femtosecond Ti:sapphire laser pulses. Thus, Talebpour *et al.* [6] and Guo *et al.* [7] have found that although as before the ionization signal for  $N_2$  remains comparable to that of its companion Ar atom, the signal for the  $O_2$  molecule is greatly suppressed compared to that of its companion noble gas Xe atom [ $E_{\text{ion}}(\text{Xe})/E_{\text{ion}}(\text{O}_2) = 12.13 \text{ eV}/12.07 \text{ eV} = 1.005$ ]. In fact the suppression for  $O_2$  ionization turns out to be more than an order of magnitude. Considerable interests have been generated by this unexpected finding. Talebpour *et al.* [6] suggested a possible reduction of the ionization signal due to a laser induced dissociative recombination. Such a laser induced recombination of the electron is generally expected to be strongly polarization dependent (cf., e.g., [8]). Guo *et al.* [7] measured the ion signals using both linear and circular polarizations of the laser field, but found that the said suppression of ionization of  $O_2$  occurs *independently* of the polarization of the field. They concluded that the difference cannot be due to dissociative recombination but should lie in the electronic structures, and suggested that a closed-shell molecule, like  $N_2$ , can be expected to behave like a noble gas atom, but not a molecule with a half-filled open-shell structure, like  $O_2$ . Another difference between a closed-shell and an open-shell species is a change of the multiplicity of the ground state, e.g., from

a singlet to a triplet state. Since an optical (dipole) field does not effectively couple to the spin degrees of freedom, it seems unlikely that a difference arising from the spin states could make such a large difference in the ionization signals of interest. In this Letter we report the results of investigations of an alternative route to answer the puzzle of the suppressed ionization in  $O_2$ , and its absence in  $N_2$ . It is shown below that the phenomenon arises from a symmetry dependent dynamical effect on the laser induced ionization process, independently of the closed- or open-shell electronic structures.

We first note that, quite generally, the valence orbital of a homonuclear diatomic molecule with an antibonding symmetry character (e.g.,  $O_2$ ,  $\pi_g$  symmetry) is very differently distributed in space than that of a molecule having a bonding symmetry character (e.g.,  $N_2$ ,  $\sigma_g$  symmetry). For the two types of homonuclear diatomic molecules, the wave functions of the valence orbitals are of the form (expressed in the convenient LCAO-MO form, e.g., [9,10]; atomic units,  $e = m = \hbar = 1$  are used below)

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

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,  $a_i = b_i$ , while, in contrast, for an antibonding orbital ( $\sigma_u$  or  $\pi_g$ ), they have the opposite sign,  $a_i = -b_i$ . This leads in the case of the antibonding symmetry to a cancellation of electron density near the central region between the nuclei and along the nuclear axis, while, in the case of the bonding symmetry, there is considerable electron density in this region. In Fig. 1 we plot the electron densities of the  $\sigma_g$  orbital of  $N_2$  and that of the  $\pi_g$  orbital of  $O_2$ , along the molecular axis ( $z$  axis) and perpendicular to it ( $\rho$  axis). They clearly exhibit the characteristic difference mentioned above. We show below that this

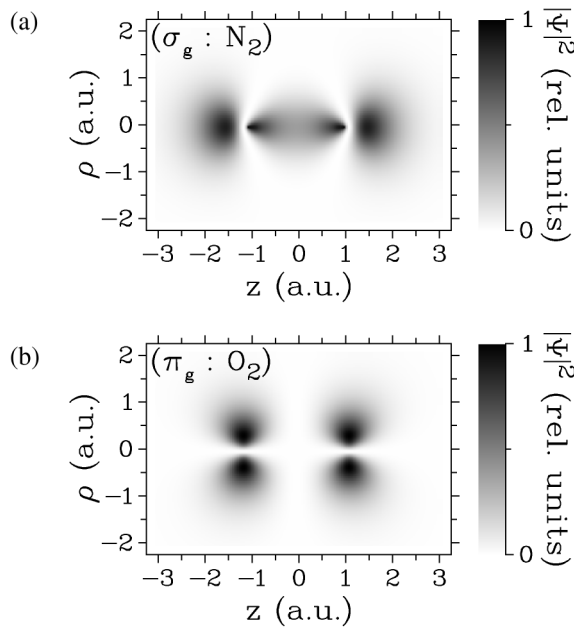


FIG. 1. Electron density in the valence orbital of (a)  $N_2$  (bonding,  $\sigma_g$  symmetry), and (b)  $O_2$  (antibonding,  $\pi_g$  symmetry), plotted along the molecular axis ( $z$  axis) and perpendicular to it ( $\rho$  axis).

difference between the two kinds of orbitals also leads to an effective destructive interference in the electron emission probability for a homonuclear diatomic molecule with an antibonding symmetry (e.g.,  $O_2$ ), and a constructive interference for a homonuclear diatomic molecule having a bonding symmetry (e.g.,  $N_2$ ).

Given the initial molecular wave function, the ionization dynamics can be simulated exactly for the  $H_2^+$  molecular ion or similar one-electron systems (e.g., [11]). Unfortunately, however, such exact simulations are practically impossible at present for molecular systems with many electrons, such as  $N_2$  or  $O_2$ . As an alternative approximate means of theoretical analysis of the ionization dynamics, therefore, we use a generalization of the so-called intense-field many-body  $S$ -matrix theory (IMST) [12], developed originally in the atomic case, to the molecular case [13]. The rates of ionization of the present interest can be obtained explicitly from the leading term of IMST that is analogous [13,14] to the so-called KFR (or Keldysh-Faisal-Reiss) model [15–17]. The KFR approximation, with a WKB correction for the final state Coulomb effect, e.g., [18,19], has been well tested against the experimental data [19] for laser induced ionization of noble gas atoms. This approximation involves the transition matrix element between the ground electronic state of the molecule, and the final bound state of the molecular ion and the Volkov (field dressed) continuum state of the emitted electron (cf. [13,14]). More explicitly, the rate of ionization (per species), in a linearly polarized laser field, for a diatomic homonuclear molecule with  $N_e$  equivalent electrons in a bonding or in an antibonding valence orbital

takes the following form [20]:

$$\Gamma^+ = N_e \sum_{N=N_0}^{\infty} \int d\hat{\mathbf{k}}_N \left( \frac{dW^{(N)}}{d\hat{\mathbf{k}}_N} \right)_{\text{at}} \times 4 \begin{cases} \cos^2(\mathbf{k}_N \cdot \mathbf{R}/2): & \text{bonding} \\ \sin^2(\mathbf{k}_N \cdot \mathbf{R}/2): & \text{antibonding}, \end{cases} \quad (2)$$

where

$$\left( \frac{dW^{(N)}}{d\hat{\mathbf{k}}_N} \right)_{\text{at}} = 2\pi C_{\text{coul}} k_N (U_p - N\omega)^2 J_N^2 \left( \boldsymbol{\alpha}_0 \cdot \mathbf{k}_N, \frac{U_p}{2\omega} \right) \times \left| \sum_{i=1}^{i_{\text{max}}} a_i \langle \mathbf{k}_N | \phi_i \rangle \right|^2 \quad (3)$$

and

$$C_{\text{coul}} = \left( \frac{2\kappa_{\text{ion}} E_{\text{ion}}}{E_0} \right)^{2Z/\kappa_{\text{ion}}}$$

is a correction factor that accounts for the final state Coulomb interaction of the Volkov electron with the residual ion [21], 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.  $J_n^2(a; b)$  is a generalized Bessel function of two arguments that arises from the Fourier decomposition of the Volkov wave function, e.g., [22];  $k_N^2/2 = N\omega - (U_p + E_{\text{ion}})$  is the kinetic energy of the electron on absorbing  $N$  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  $E_{\text{ion}} \equiv \kappa_{\text{ion}}^2/2$  is the ionization energy of the molecule [23].

Before proceeding further, it is interesting to briefly consider the formal structure of the above rate formula. Equation (2) shows that the rate of ionization of a homonuclear diatomic molecule, for any number of photon absorption, essentially factorizes into that of an atomlike (“atom in molecule”) part, Eq. (3), and a trigonometric part associated with an interference effect between the waves of the ionizing electron centered about the two nuclei. In the case of molecules with valence orbitals of antibonding symmetry, one may expect that the interference term would tend to behave destructively (while that for the bonding symmetry, constructively), since for a small argument ( $\mathbf{k}_N \cdot \mathbf{R}/2$ ), which corresponds to the first few and dominant photon orders  $N$  [24],  $\sin^2(\mathbf{k}_N \cdot \mathbf{R}/2) \ll 1$  and  $\cos^2(\mathbf{k}_N \cdot \mathbf{R}/2) \approx 1$ . To check this expectation we have carried out detailed calculations of the ionization rates for  $N_2$  and  $O_2$ , using Eqs. (2) and (3), as well as that of their companion atoms, Ar and Xe. For the atomic case, the corresponding formula for the rate of ionization of the noble gas atoms [19] has been used. The ground state wave functions for the closed-shell and the open-shell 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 [25]. The basic rates of ionizations so obtained are then employed to compute the total ion yields assuming a

Gaussian laser beam (TEM<sub>00</sub> mode) and also a Gaussian pulse profile, having the same beam waist and pulse duration as that used in the experiments [6,7]. Finally, the calculated yields are orientation averaged assuming random orientations of the molecular axis with respect to the laser polarization axis [26].

Results are obtained for laser parameters as in the experiments by Guo *et al.* [7] and Talebpour *et al.* [6], who used femtosecond Ti:sapphire lasers at  $\lambda = 800$  nm, and pulse durations of 30 and 200 fs, respectively. For the sake of direct comparison with these relative experimental data, we have matched the theoretical value and the data at *one* point only, namely, at the saturation intensity of the corresponding companion atom. We may emphasize that this automatically fixes the scale for the companion molecule also, for all intensities.

In Fig. 2 the experimental ion signals (upper panel) for the pairs N<sub>2</sub> and Ar, and O<sub>2</sub> and Xe, measured by Guo *et al.* [7], and the corresponding theoretical results (lower panels) are presented. The experimental data clearly show the phenomenon of “suppressed ionization” for O<sub>2</sub>, as we mention at the outset, and its absence in the case of N<sub>2</sub>. The same behavior is reproduced here also by the present theoretical calculations [28]. In Fig. 3 we compare the results of the experiments of Talebpour *et al.* [6] (upper panels) with that of the present calculations (lower panels).

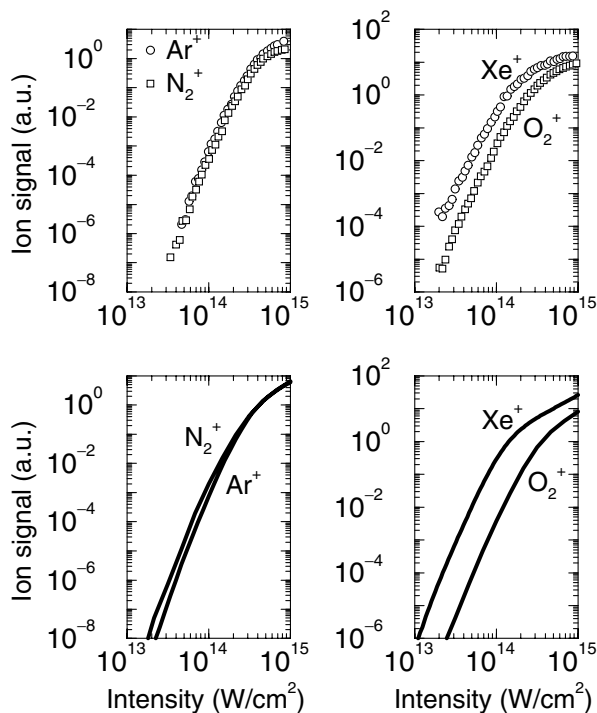


FIG. 2. Suppressed molecular ionization of O<sub>2</sub> [7] (upper panels), compared to that of its companion noble gas Xe atom and its absence in N<sub>2</sub>, compared to its companion Ar atom. Results of present calculations for the respective pairs are shown in the lower panels. Laser parameters (in experiments and calculations):  $\lambda = 800$  nm,  $\tau = 30$  fs.

Again we see a similar suppression of ionization of O<sub>2</sub> by more than an order of magnitude, in both experimental and theoretical signals, compared to that of Xe. Thus the present calculations are found to be qualitatively consistent with the observations of suppressed ionization of O<sub>2</sub> in both the experiments. We note that the calculated yields for N<sub>2</sub>, unlike that of the data, somewhat overestimate that of Ar. This is probably due to the quantitative limitation of the present model based on the lowest order IMST that remains to be investigated in the future.

Finally, we consider the ionization yields of the diatomic F<sub>2</sub> and compare it directly with N<sub>2</sub>, its *molecular* companion [ $E_{\text{ion}}(\text{F}_2)/E_{\text{ion}}(\text{N}_2) = 15.69 \text{ eV}/15.58 \text{ eV} = 1.01$ ]. This case is particularly interesting in that F<sub>2</sub> has the same spatial symmetry (antibonding,  $\pi_g$ ) as O<sub>2</sub>, but it has a closed-shell (singlet) ground state, as opposed to the open-shell (triplet) ground state of O<sub>2</sub>, considered above. In Fig. 4 we present the results of calculations for F<sub>2</sub> and compare them with that of N<sub>2</sub> (bonding,  $\sigma_g$  symmetry), for the same laser parameters as in the experiments for N<sub>2</sub>, discussed above. From the spatial symmetry argument made at the outset one expects *a priori* that the ionization signal from F<sub>2</sub> ought to be suppressed with respect to its companion molecule N<sub>2</sub>. This expectation is well corroborated by the calculated ionization yields shown in Fig. 4. Thus, not only the molecule O<sub>2</sub> but also F<sub>2</sub> can exhibit the phenomenon of suppressed ionization, independently of their closed- or open-shell structure and/or the multiplicity. We finally note that a generalization of the present

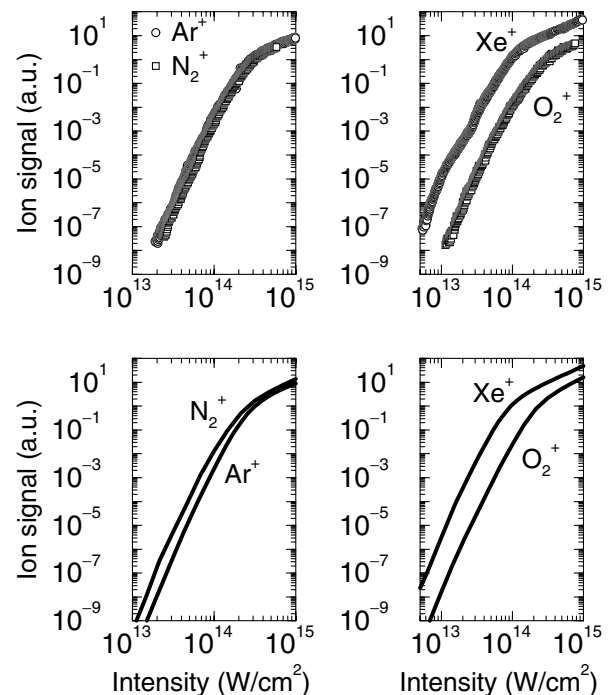


FIG. 3. Same as in Fig. 2, except pulse duration,  $\tau = 200$  fs; experimental observations of Talebpour *et al.* [6] (upper panels); present model calculations (lower panels).

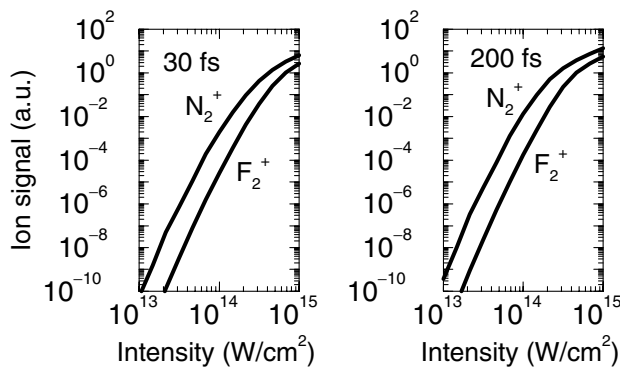


FIG. 4. Theoretical calculations showing suppressed ionization of  $F_2$  (closed-shell, antibonding,  $\pi_g$  symmetry) in comparison with its *molecular* companion  $N_2$  (closed-shell, bonding,  $\sigma_g$  symmetry). The laser parameters are  $\lambda = 800$  nm,  $\tau = 30$  fs (left panel), and  $\tau = 200$  fs (right panel).

symmetry induced dynamical effect can provide an understanding of suppressed ionization of larger symmetric polyatomic molecules too [29].

To conclude, both symmetry considerations and direct model calculations in specific cases of the ionization signals show that the *class* of homonuclear diatomic molecules that has active valence orbitals with antibonding symmetry ( $\pi_g, \sigma_u$ ) can exhibit the phenomenon of “suppressed” molecular ionization in intense femtosecond laser fields. The experimental data that exhibit ionization suppression of  $O_2$  and its absence in  $N_2$  are analyzed and found to be consistent with the above interpretation. A similar suppression of ionization for the closed-shell molecule  $F_2$ , compared to that of its *molecular* companion  $N_2$ , is also predicted to occur.

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