Ionization Suppression of Diatomic Molecules in an Intense Midinfrared Laser Field

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(Received 8 November 2011; published 29 May 2012)

Diatomic molecules (e.g., O_2) in an intense laser field exhibit a peculiar suppressed ionization behavior compared to their companion atoms. Several physical models have been proposed to account for this suppression, while no consensus has been achieved. In this Letter, we aim to clarify the underlying mechanisms behind this molecular ionization suppression. Experimental data recorded at midinfrared laser wavelength and its comparison with that at near-infrared wavelength revealed a peculiar wavelength and intensity dependence of the suppressed ionization of O_2 with respect to its companion atom of Xe, while N_2 behaves like a structureless atom. It is found that the *S*-matrix theory calculation can reproduce well the experimental observations and unambiguously identifies the significant role of two-center interference effect in the ionization suppression of O_2.

DOI: 10.1103/PhysRevLett.108.223001 PACS numbers: 33.80.Rv, 33.80.Wz, 42.50.Hz

Ionization of molecules in intense laser pulses plays a central role in understanding strong field molecular physics. Most molecular strong field processes, such as above-threshold ionization, high-harmonic generation, double ionization, and Coulomb explosion are derived directly from this fundamental process. Compared to atoms, for which the ionization and related phenomena have been well understood [1], molecular ionization exhibits a large variety of peculiar behaviors due to its structural complexity and the extra nuclear degrees of freedom [2].

One of the most fundamental differences between a molecule and its companion atom, i.e., the atom with a comparable ionization potential, is represented by their relatively distinct ionization probability. For example, when subject to a Ti:sapphire laser pulse at ~800 nm, a strong suppression has been observed in ionization probability of diatomic molecule O_2 compared to the rare gas atom Xe, while no suppression is seen in the diatomic molecule N_2 compared to its companion atom Ar [3,4]. Several theoretical models, including the Keldysh-Faisal-Reiss [5], multielectron screening [6], or MO-ADK [molecular version of the Ammosov-Delone-Krainov (ADK)] [7] models, have been proposed to address this issue. The Keldysh-Faisal-Reiss model predicts that the interference between ionizing wave packets emitted from the two distinct nuclear centers can lead to ionization suppression for molecules (e.g., O_2) with antisymmetric electronic ground states. The multielectron screening model introduces a charge-screening correction to the tunneling theory. In the MO-ADK model, the difference between atomic and molecular ionization is attributed to different asymptotic behaviors of their ground state wave functions [7]. Though all the proposed models can, in principle, account for the experimental observations, mostly at the near-infrared wavelength of 800 nm, no consensus on the underlying mechanism has been achieved so far. In fact, though these models are substantially different in many aspects and led to different viewpoints of the strong field molecular ionization process, all the models, especially the MO-ADK model [8–10] and Keldysh-Faisal-Reiss model [11–16], have been extensively employed to investigate the ionization process of molecules mainly in the tunneling regime. In addition, various *ab initio* methods have also been applied to study this problem, and qualitative agreement with the experimental results has been achieved [17–19]; however, no clear physical mechanism can be identified. Recently, alignment dependence of molecular ionization has been measured, and the comparison with theories [20] shed more light on the underlying molecule specific effects and demonstrated the significance of the orbital symmetry of the molecules in their ionization dynamics.

Further understanding and clarification of the mechanism behind the distinct molecular ionization requires, from an experimental point of view, the extension of the measurements into other wavelength ranges than solely 800 nm. Indeed, a recent experiment performed at a shorter wavelength of 400 nm [21] exhibited a similar behavior of O_2 and, however, a rather disparate behavior of N_2. The latter is found to have a higher ionization probability compared to that of Ar for linear polarization, while the difference vanishes for circular polarization. This has been explained by the resonance enhancement, a characteristic of multiphoton ionization process, in N_2. On the other side, this multiphoton ionization resonance effect may also contribute significantly to the atomic or molecular ionization at 800 nm [22], frustrating an explicit comparison with the theory and a clear identification of the mechanism.

In this Letter, we perform a comparison study of intense field ionization between diatomic molecules (i.e., N_2 and O_2) and their companion atoms (i.e., Ar and Xe) at a midinfrared wavelength of 2000 nm. In contrast to previous studies carried out at shorter laser wavelengths, our experiment at this long wavelength ensures that the ionization process falls deeply within the tunnel ionization regime [23,24]. The comparison of the data with the theory provides a crucial clue to the physical mechanism behind molecular ionization in the tunnel ionization regime, which is of special importance to the emerging field of ultrafast imaging of molecular structure and dynamics, wherein the ionized electrons from the molecules can be employed as a tool in imaging of molecular orbitals [16,25,26] and probing nuclear dynamics with attosecond resolution [27].

In our experiments, wavelength-tunable midinfrared femtosecond laser pulses are generated by an optical parametric amplifier (TOPAS-C, Light Conversion, Inc.) pumped by a commercial Ti:sapphire laser system (Legend, Coherent, Inc.). This optical parametric amplifier system has been described in detail elsewhere [28]. The pulse energy from the optical parametric amplifier is variable, before focused into the vacuum chamber, by means of an achromatic half-wave plate followed by a polarizer. A standard time-of-flight mass spectrometer is used to register the ion signal. By means of a cryopump, the base pressure of the spectrometer is maintained below 10^{-8} mbar. At the end of the spectrometer, ions are detected with a microchannel plate as a function of flight time. The ion signal is further amplified, discriminated, and sent to a multihit time digitizer to generate time-of-flight mass spectra. Depending on the laser intensity, the data point in the ion yield plots is obtained by averaging over 10^4 up to 6×10^6 laser shots at each intensity to ensure a sufficiently high statistical accuracy.

In Figs. 1(a) and 1(b), we present the measured ion yields of singly charged O_2 versus Xe and N_2 versus Ar, respectively, using a linearly polarized light at a center wavelength of 2000 nm. For comparison, data recorded at a Ti:sapphire laser wavelength of 800 nm are also shown in the inset. Very similar to previous studies at only 800 nm [4], our data show that N_2 and Ar have parallel ionization probabilities also at 2000 nm, while for O_2, a significant suppression of ionization yield compared to Xe is found for both 800 and 2000 nm fields.

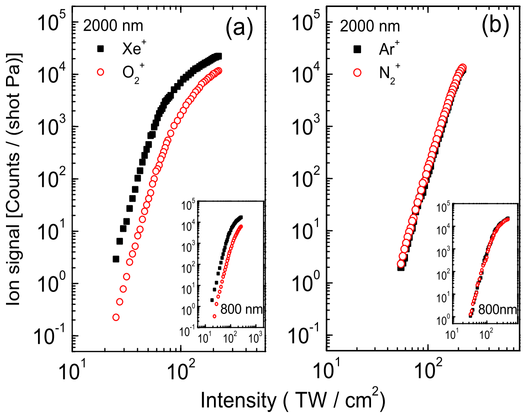

FIG. 1 (color online). Experimental single ionization yields of diatomic molecules (i.e., O_2 and N_2) and their companion atoms (i.e., Xe and Ar) as a function of laser intensity at 2000 nm. The corresponding data recorded at 800 nm are also shown in the inset for comparison.

In order to compare quantitatively the relative ion yields of the molecules with respect to their companion atoms and to provide more information for the benefit of understanding the underlying mechanism, we plot the ratio of ionization yield of O_2 with respect to Xe in Fig. 2(a) and N_2 with respect to Ar in Fig. 2(b), respectively. It is found that the ratio of N_2^+/Ar^+ keeps almost constant, to be around 1, suggesting that the N_2 always behaves like a structureless atom, irrespective of the laser intensity and wavelength. On the other side, the ratio of O_2^+/Xe^+ shows a strong dependence on the laser intensity. The ratio gradually increases with increasing intensity in both the 800 and 2000 nm cases. More interestingly, the ratio shows a clear wavelength dependence. The two ratios almost coincide at about the lowest intensity used in the experiment, but the ratio of 2000 nm apparently increases faster with intensity than that of 800 nm, which indicates that, for the same intensities above $5\text{–}6 \times 10^{13}$ W/cm^2, the longer the wavelength, the less pronounced ionization suppression of O_2 compared to Xe.

This apparent dependence of the ratio of O_2^+/Xe^+ on the laser wavelength is inconsistent with the MO-ADK model

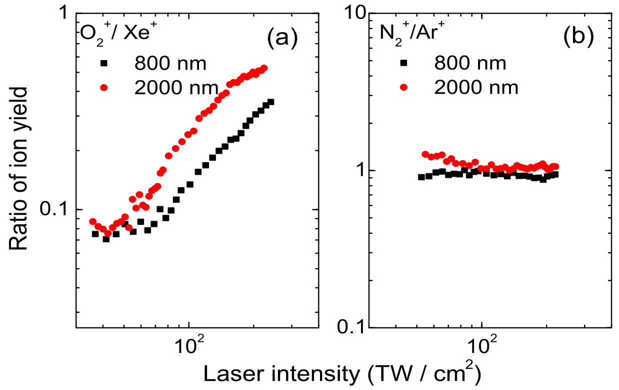

FIG. 2 (color online). Experimental ratios of ionization yield between molecules and their companion atoms for both 800 and 2000 nm, as a function of laser intensity.

prediction [7], since the ADK-type tunneling formulation is based on a quasistatic approximation which will give an ionization rate independent of the wavelength. On the other side, the multielectron screening model predicts that the suppression of the O_2 compared to Xe should be more pronounced with the increase of the laser wavelength [6,21], which is also in disagreement with the experimental observations. In contrast, we will see below that this dependence of the ratio of O_2^+/Xe^+ on both the wavelength and the intensity can be well understood within the S-matrix formulation and is closely related to the destructive interference of the two subwaves of the ionizing electron emerging from the two atomic centers of O_2 with a ground state of antibonding symmetry.

In the S-matrix theory, the single ionization rate for an atom or a molecule in a linearly polarized laser field with a vector potential $\mathbf{A}(t) = A_0 \mathbf{e}_z \cos(\omega t)$ is given by [5,29]

$$W = 2\pi N_e \sum_{N=N_0} k_N (U_p - N\omega)^2 \int d\hat{k}_N J_N^2 \times \left(\mathbf{k_N} \cdot \alpha, \frac{U_p}{2\omega}\right) |\langle \phi_{k_N}(\mathbf{r}) | \psi_i(\mathbf{r}) \rangle|^2. \tag{1}$$

Here N_e denotes the number of equivalent electrons, and N_0 is the minimum number of the photons needed to ionize the target. $k_N = \sqrt{2(N\omega - I_p - U_p)}$, and $\mathbf{k}_N$ represents the momentum of the emitted electron, with I_p and U_p the ionization potential and ponderomotive energy, respectively. J_N is a generalized Bessel function with $\alpha = A_0 \mathbf{e}_z/\omega$. $\phi_{k_N}(\mathbf{r})$ denotes the plane wave function, and $\psi_i(\mathbf{r})$ is the ground state wave function of the atom or molecule. In our calculation, the wave function of atomic ground state is approximated by the outmost single electron orbital, while for molecules we use the linear combination of atomic orbitals to simulate the molecular orbital approximately [13,30]. Moreover, according to *ab initio* calculation using time-dependent density-functional theory in Ref. [19], the highest-occupied molecular orbital (HOMO) ($1\pi_g$) dominates in the ionization process of O_2 molecule, while both HOMO ($3\sigma_g$) and HOMO-1 ($1\pi_u$) play an important role for N_2. Therefore, only HOMO is considered for O_2, and both HOMO and HOMO-1 are considered for N_2 in our calculation.

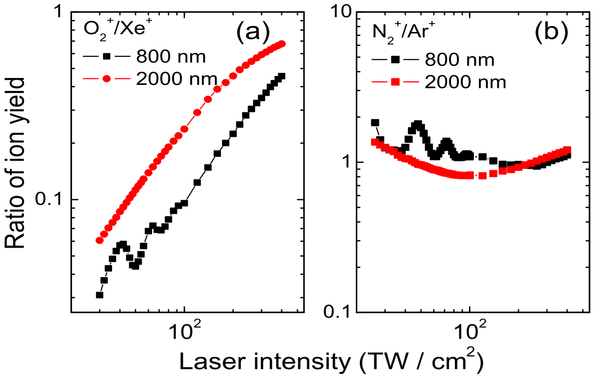

FIG. 3 (color online). Ratios of ionization yield between molecules and their companion atoms for both 800 and 2000 nm, calculated from the S-matrix theory, as a function of laser intensity.

The calculated ratio of single ionization rates for molecules O_2 and N_2 with respect to their companion atoms Xe and Ar as a function of laser intensity at 800 and 2000 nm is shown in Figs. 3(a) and 3(b), respectively. It is found that the theoretical results are well consistent with the experimental data [31]. The ratios for N_2^+/Ar^+ keep around 1, irrespective of the field intensity and wavelength. In contrast, the ratios for O_2^+/Xe^+ show strong suppression and raise with the increase of the laser intensity. Moreover, the ratio of 2000 nm keeps higher than that of 800 nm for the whole intensity regime considered. Especially, both experimental and theoretical data agree on that the ratio of O_2^+/Xe^+ depends linearly on the laser intensity (i.e., $\propto I$); e.g., the ratio of 800 nm increases by about 4 times when the laser intensity increases by about 4 times [see Fig. 2(a)]. It is noteworthy that this amount of increase is significantly larger than that predicted by the MO-ADK theory, which gives a scaling of $I^{1/2}$ [7].

Further comprehension of the distinct intensity and wavelength dependence of the ratio of O_2^+/Xe^+ can be drawn from the S-matrix formula, in which the single ionization rate of molecules consists of two major parts that come from the Fourier transform of the ground state. For O_2, the Fourier transform has the form $\Psi_i(\mathbf{k}_N) = C\Phi_{\text{at}}(\mathbf{k}_N) \sin(\mathbf{k}_N \cdot \mathbf{R}/2)$ with C being the normalization factor. Here $\Phi_{\text{at}}(\mathbf{k}_N)$ is the atomlike part, which is determined mainly by the atomic orbital constituting the molecular orbital ($2p_x$ wave function for O_2), and the trigonometric part $\sin(\mathbf{k}_N \cdot \mathbf{R}/2)$ depends on the molecular structure and is associated with the interference effect between the wave packets of the ionizing electrons centered at the individual nucleus [5]. This trigonometric part leads to the suppression effect, since it always gives destructive interference when $\mathbf{k}_N \cdot \mathbf{R} \ll \pi$, which is usually well satisfied considering the fact that the vast majority of ionized electrons have small momenta.

This suppression effect can be clearly seen in Fig. 4(a), which shows the calculated ion yield ratio between the two cases with and without the trigonometric term included in Eq. (1), denoted by O_2^+ and O_2^{+*}, respectively, for both 800 and 2000 nm laser wavelengths. When the trigonometric term is included, the ionization yield is significantly suppressed. Moreover, the ratio ascends with intensity and increases with laser wavelength. To understand these effects, we plot the momentum spectra of photoelectrons emitted from the ionization of molecular O_2, calculated without the trigonometric term, for different laser intensities and wavelengths. As shown in Figs. 4(b) and 4(c), calculated at 800 and 2000 nm, respectively, the contribution from large k_N becomes more significant as the

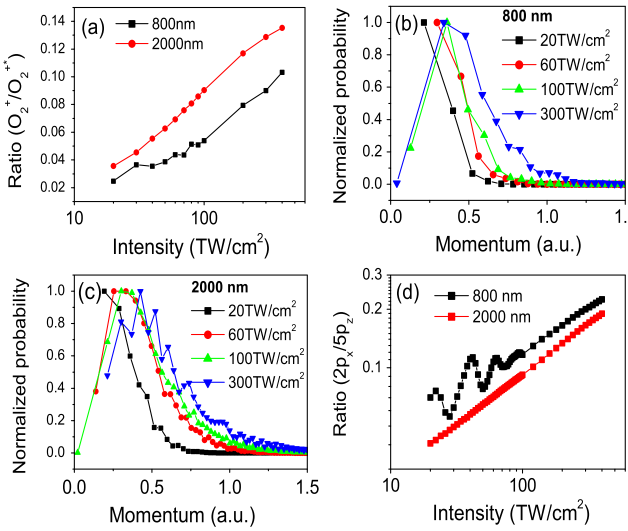

FIG. 4 (color online). (a) Calculated ratio between the ionization yield of O_2 with (denoted as O_2^+) and without the trigonometric term (denoted as O_2^{+*}) (see the text). (b),(c) Normalized momentum spectrum of the photoelectron from O_2 calculated without the trigonometric term at molecular alignment 45° with respect to the laser field. The field parameters used in the calculations are shown in the panels. (d) Calculated ratio between the ionization yield of an atom with orbital $2p_x$ and $5p_z$. The ionization potential is the same as that of O_2.

intensity increases. This will cause an increase of the interference term $\sin(\mathbf{k}_N \cdot \mathbf{R}/2)$ and, as a consequence, the ascending ratio with the increase of the laser intensity, in agreement with the results in Fig. 4(a). In addition, for a certain laser intensity the momentum spectrum becomes broader when the wavelength increases [comparing Fig. 4(c) with Fig. 4(b)]. Similar to the intensity effect, this results in an increasing ratio and less pronounced suppression effect for a longer wavelength, which is consistent well with the experiment. Note that in Figs. 4(b) and 4(c), for simplicity, we show only the electron distribution for a specific molecular alignment angle of 45° with respect to the field direction, since the ionization rate of O_2 reaches maximum at about this angle [16]. It is worthy to mention that the distributions are not sensitive to the alignment angle in our calculations. Therefore, the interference effect from the trigonometric term originating from the multicenter feature of molecules plays an essential role in the ionization suppression of the O_2 molecule. For the N_2 molecule, the situation is much more complicated. Besides the HOMO orbital, the HOMO-1 orbital contributes to the total ion yield and is becoming especially important at high intensities. Moreover, the HOMO orbital is an admixture of both atomic *s* and *p* orbitals. The contributions of these two types of orbitals, which possess trigonometric terms of both $\cos(\mathbf{k}_N \cdot \mathbf{R}/2)$ and $\sin(\mathbf{k}_N \cdot \mathbf{R}/2)$, add coherently in the calculation [32]. As a result, N_2^+/Ar^+ shows no suppression and is hardly dependent on the laser wavelength.

Note that the ratio of O_2^+/Xe^+ has a scaling of $\propto I$ dependence on the laser intensity [see Figs. 2(a) and 3(a)], in contrast to that the ratio shown in Fig. 4(a), introduced solely by the interference effect, gives a scaling of $\propto I^{1/2}$. The other contribution accounting for the additional $I^{1/2}$ comes from the effect of the atomic orbitals. It is noteworthy that the outmost orbital of the O_2 molecule is composed of a $2p_x$ orbital, while the outmost orbital of the xenon atom is $5p_z$. As shown in Fig. 4(d), our calculation shows that the ratio between the ionization yield from these two orbitals will also increase by about 3–4 times when the intensity increases by about 1 order of magnitude, which gives an additional $I^{1/2}$ dependence of the ratio O_2^+/Xe^+. Therefore, the two-center interference effect, together with the atomic orbital effect, gives rise to the experimentally observed intensity dependence ($\propto I$) of the O_2^+/Xe^+.

A closer comparison between our theoretical simulation [Fig. 3(a)] and experimental data [Fig. 2(a)] shows a perceptible discrepancy at a very low intensity regime. The experimental ratio does not decrease with decreasing intensity, while the theoretical ratio keeps dropping below $4–5 \times 10^{13}$ W/cm^2. This discrepancy may be partially attributed to the resonance effect that becomes important when the laser intensity is low and the ionization is well in the multiphoton regime [21]. In the multiphoton regime, the ionization channel via the Freeman-resonance process [33] contributes significantly to the ionization yield. It is well known that the O_2 molecule possesses more abundant highly excited states than Xe and hence provides more resonance channels for the above-threshold ionization process, resulting in the increased ratio of O_2^+/Xe^+ compared with that given by the *S*-matrix calculation in which all the resonance processes are ignored.

In summary, we present a comparison study on the ionization of diatomic molecules (N_2 and O_2) and their companion atoms (Ar and Xe) at a midinfrared wavelength. Our experimental data reveal that the ionization probability of N_2 is almost identical to its companion atom of Ar, irrespective of laser wavelength and intensity. In contrast, O_2 exhibits a distinct suppression compared to Xe, and, more importantly, a strong dependence of this suppression on both the laser wavelength and intensity has been found. While this finding is in conflict with the molecular ADK formulation and multielectron screening model predictions, it can be well reproduced by the *S*-matrix theory calculation. Our analysis unambiguously shows that the effect of interference between ionizing wave packets emitted from the two ionic cores, which is inherently included in the *S*-matrix theory, plays an essential role in the ionization process of diatomic molecules. This interference effect, together with the different intensity dependence of the ionization of atomic orbitals, accounts for the peculiar ionization behavior of O_2 compared to its companion atom Xe. Moreover, it is noteworthy that the molecular ADK model, which has been widely used in the study of the molecular ionization process in the tunneling regime, is actually incapable of describing the ionization process of the oxygen molecule, remarkably in contrast to our previous understanding of the molecular ionization process.

This work is supported by NNSF of China (Grants No. 10925420, No. 11134010, No. 10904162, No. 11074026, No. 11104225, No. 60825406, and No. 11174330) and the National Basic Research Program of China Grant No. 2011CB8081002.

Note added in proof.—Recently, a paper by J. Durá *et al.* [34] was published, which addresses similar questions.

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