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Ellipticity effects on single and double ionization of diatomic molecules in strong laser fields

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By studying high-precision ion yield measurements in diatomic molecules N_2 and NO with 30-fs linearly (LP) and circularly (CP) polarized light, we extend to molecular systems the study of ellipticity effects on both single and double ionization in strong laser fields. Competing ionization rates between LP and CP light, as predicted in the Ammosov-Delone-Krainov model, is observed experimentally by studying singly ionized N_2 and NO. We further observe an anomalously high NO^{2+} signal with CP, which shows a nonsequential ionization signature. A hypothesis is given that ties this observation to the influences of electronic structure on ellipticity effects in strong-field ionization.

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The understanding of photoionization is the foremost problem in strong-field atomic and molecular physics, since most of the phenomena currently studied, such as single and multiple ionization, above-threshold ionization, high-order harmonic generation, molecular dissociation and ionization, and photoelectron spectroscopy, are derived directly or indirectly from electron ionization [1]. Among various properties associated with ionization processes in atoms and molecules, the study of ellipticity effects constitutes one important aspect in studying the dependence of ionization behavior on field polarization.

Ellipticity effects on single and double ionization, high-order harmonic spectra, and photo-electron angular distributions have been studied in rare-gas atoms [1,2]. For strong-field ionization, tunneling plays an important role in both single and double ionization: in the tunneling regime [3], single and sequential double ionization of rare-gas atoms are well described by the Ammosov-Delone-Krainov (ADK) tunneling model [4], and ellipticity effects on the strong-field tunneling ionization follow the predication of the ADK model. For nonsequential double ionization (NSDI) [5–7], ellipticity is one of the most important factors in influencing the yield, where the NSDI rate is relatively high for linear polarization but appears to be completely suppressed with circularly polarized light [6]. However, these properties are established mainly on the basis of the extensive study of the rare-gas atoms that all have similar closed-shell electronic structures.

In contrast to the relatively well studied ellipticity effects in rare-gas atoms, almost no work has been devoted to studying ellipticity effects in molecules due to the complexity of the extra degrees of freedom. However, molecules can potentially provide important tests of strong-field dynamics, since even easily studied diatomic molecules have a greater diversity of electronic structures. Recently, detailed electronic structure has been demonstrated to play an essential role in influencing a variety of strong-field phenomena, such as single and double ionization, NSDI, charge asymmetric dissociation, molecular fragmentation, and strong-field dynamics [8–12]. Motivated by these established experimental and theoretical studies, we set out to study ellipticity effects on strong-field ionization in molecules by considering the importance of electronic structure.

In this paper, by eliminating the effects of enhanced ionization of molecules at critical internuclear separations by using 30-fs ultrashort pulses [9,10,13], we study the ionization behavior of diatomic molecules N_2 and NO with both linearly (LP) and circularly polarized (CP) light. As a closed-shell molecule, N_2 is compared to the rare-gas atom Ar, both of which have a similar electronic structure as well as single and double ionization potentials. In contrast, the so-called ''hydrogenlike molecule,'' NO, has a closed-shell structure plus one $\pi_g 2p$ valence electron resembling the electronic structure of the hydrogen (H) atom. Although there is no direct experimental study on the H atom, an attempt is made to find some underlying similarity between our experimental results and *ab initio* calculations on the H atom.

The laser used in the experiment is an amplified Ti:sapphire system running at a 1-kHz repetition rate, producing over 400 μJ/pulse in 30-fs pulses with a central wavelength of 800 nm [14,15]. The experimental setup and techniques closely follow those described in Refs. [8,10]. Briefly, ion signals are studied with a standard time-of-flight (TOF) mass spectrometer [16]. High-precision ionization yield measurements in different molecular species are essential in order to study ionization in molecules. Using a technique introduced in Ref. [10], we are able to accurately determine the flight time and width of a certain species in the TOF signals to isolate them from contamination from adjacent TOF peaks.

High-precision ion yield measurements of singly and doubly ionized N_2, Ar, and NO are shown in Figs. 1 and 2. N_2 and Ar have almost the same single- and double-ionization potentials (N_2, 15.58 and 27.12 eV; and Ar, 15.76 and 27.63 eV), and we can see that single- and double-ionization yields of N_2 and Ar using both LP and CP are very similar over the entire intensity range. Except for, of course, the NSDI component in double ionization, the N_2 and Ar data follow the prediction of the ADK model reflecting the tunneling nature of the ionization. For single ionization, there is a shift of the N_2^+ and Ar^+ ion yields along the intensity axis from LP to CP (a factor of $\sim 1.6-1.7$), which remains relatively paral-

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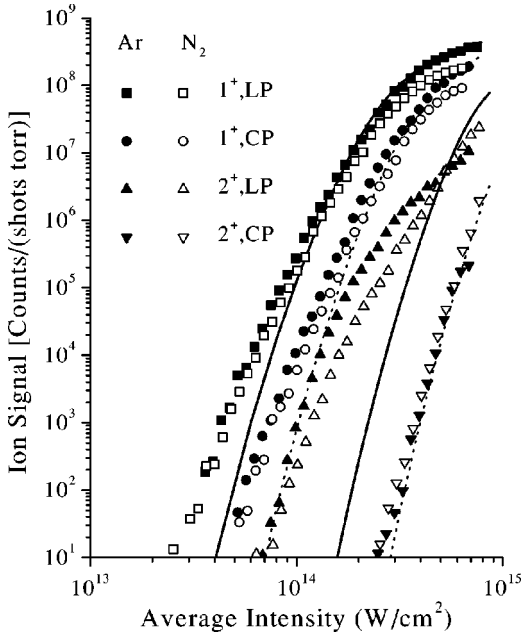

FIG. 1. Single- and double-ionization yields for N_2 and Ar using LP and CP. Calculations based on the ADK model are shown by the full (LP) and dotted (CP) curves. The N_2^+ data are slightly reduced at the highest intensities due to detector saturation.

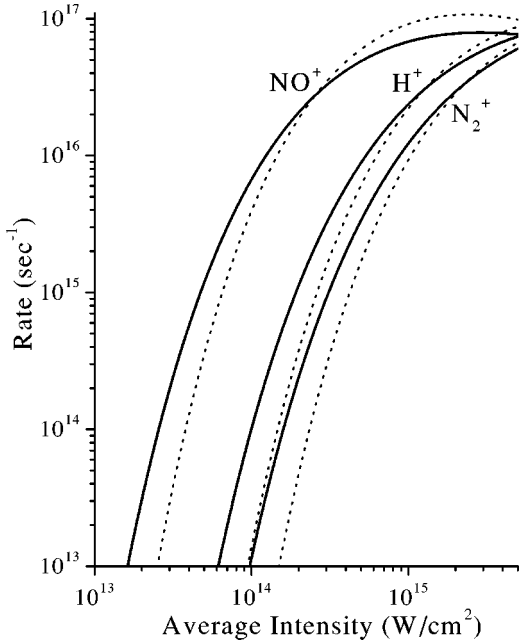

FIG. 3. Single-ionization rates, predicted by the ADK model, for N_2, NO, and H using LP (full curves) and CP (dotted curves).

lel over the entire experimental intensity range from 2×10^{13} W/cm^2 to 6×10^{14} W/cm^2. In contrast, ion yields for NO^+ between LP and CP are very close together and become almost identical at saturation intensities above 1×10^{14} W/cm^2. NO has a relatively low single ionization potential (9.25 eV); the multiphoton process dominates ionization processes below the saturation intensity. However, the ADK model still fits the data quite well at intensities above 8×10^{13} W/cm^2 (corresponding to the Keldysh parameter of 1 [3]), as shown in Fig. 2. Both the data and the model prediction indicate that the LP and CP ion yields in NO^+ approach each other and are almost identical with increasing intensity.

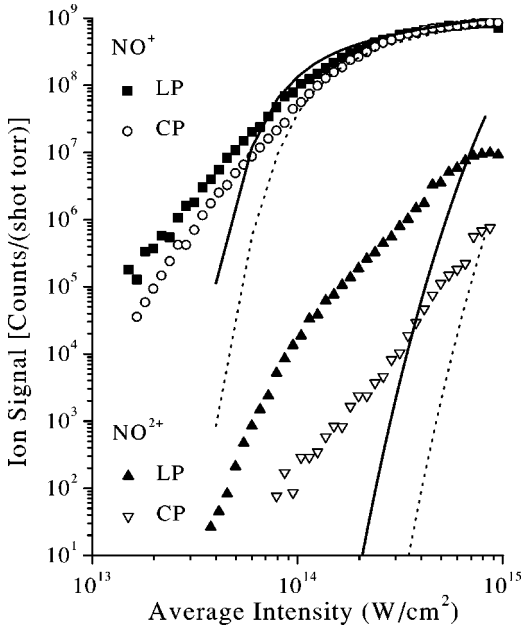

FIG. 2. Single- and double-ionization yields for NO using LP and CP. Calculations based on the ADK model are shown by the full (LP) and dotted (CP) curves.

To understand the different shift from LP to CP between N_2^+ and NO^+ in the tunneling regime, we consider the ionization rate of LP versus CP from the ADK model prediction. The ADK model first predicts the ionization rate for a static field, which is equivalent to the CP rate. The LP rate is further obtained by integrating the static rate over one optical cycle. Based on the ADK model, the ionization rate for CP is slightly higher than for LP for equal field strength, since electrons can escape from an atom at any time during the optical cycle in the direction of the instantaneous electric field. When plotted against equal average intensity (normally used in experiments), however, the ionization rate of LP is higher than that of CP for a wide range of intensity, since the instantaneous peak intensity for LP is twice the peak intensity for CP for the equal average intensity. To see this, the ionization rates of singly ionized N_2, NO, and the H atom with both LP and CP from the ADK model calculations are shown in Fig. 3. For all three species, the shift from LP to CP rate along the intensity axis ($\sim1.6-1.7$) remains relatively parallel below a certain intensity, but eventually, the ionization rate of CP surpasses that of LP with increasing intensity. Therefore, for equal average intensity, it appears that ionization is more efficient with LP for moderate intensities, but more efficient for CP at higher intensities. This interesting competing behavior between LP and CP has also been seen in recent *ab initio* quantum mechanical calculations with the H atom although the connection to the ADK model has not been pointed out there [17]. For N_2^+, our laser intensity (below 6×10^{14} W/cm^2) limits our study to

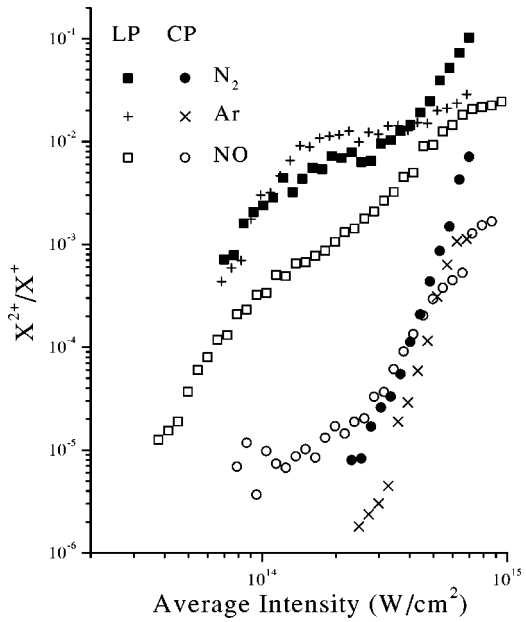

FIG. 4. Ratio curves of X^{2+}/X^{+} for N_2, Ar, and NO using LP and CP.

the range where the LP and CP rates remain nearly parallel. For NO^{+}, however, the ADK model shows that the LP and CP rates approach each other and cross at an intensity of $\sim 2\times 10^{14}$ W/cm^2, and this behavior is almost exactly reflected in our experimentally observed ionization yields for NO^{+}. (Note that after volume average, the ionization yields from the ADK model calculations will not show the crossing of the LP and CP ionization rates at the crossing intensity).

NSDI is currently one of the most challenging problems in strong-field physics, normally involving an enhancement in the double-ionization yields compared to calculations based on sequential processes. As pointed out in the introduction, a very sensitive dependence of the NSDI rate on field polarization has been found in both rare-gas atoms [6] and molecules [10]. Despite many similarities between diatomic molecules N_2 and NO, e.g., the number of electrons outside the nucleus (14 and 15, respectively) and the internuclear distance ($\sim 1.1-1.2$ Å), NSDI of NO shows an entirely different ellipticity dependence from those of N_2 and Ar. From Fig. 2, we can see that the NO^{2+} signal with CP does not fall off rapidly with decreasing intensity as in $N_2{}^{2+}$ and Ar^{2+}; instead, the ion yield of NO^{2+} with CP is relatively high at lower intensities, showing a knee structure for intensities below 3×10^{14} W/cm^2, indicating an NSDI component commonly seen in LP yields. Since the ADK model may not give an accurate fit for a non-rare-gas-like molecule [8], we use a well established technique by plotting the intensity dependence of the ratio X^{2+}/X^{+} to characterize the NSDI behavior quantitatively [7,8], where X^{+} and X^{2+} are the yields for single and double ionization of some atom or molecule X. In Fig. 4, ratio curves of $N_2{}^{2+}/N_2{}^{+}$ and Ar^{2+}/Ar^{+} with LP show weak intensity dependencies at intensities below 3×10^{14} W/cm^2, indicating an NSDI component [8]. However, the ratio curves for N_2 and Ar with CP drop significantly with decreasing intensity and do not show the NSDI behavior [8,10]. In contrast, there is clearly a flat part in the NO ratio curve with CP below the intensity of $\sim 3\times 10^{14}$ W/cm^2 that exceeds the N_2 and Ar counterparts despite the LP ratio in NO showing a much weaker NSDI rate compared to those in N_2 and Ar. (The NSDI behavior with LP in NO agrees with that observed in Ref. [18]). Note that our comparison is based on comparing the LP and CP ratios of NO to their counterparts in N_2 and Ar (as a reference) instead of comparing between the LP and CP ratios of NO itself. Therefore, there appears to exist an NSDI-like component in NO^{2+} with CP.

The rescattering model has been proposed to explain NSDI and the associated ellipticity effects [19]. The model states that an electron can collide with its parent ion core at least one-half cycle after being driven away by a laser field, and this e-2e rescattering could lead to an enhanced two-electron simultaneous emission. The probability for an electron to rescatter off its atomic parent core will be greatly reduced in a CP field, since there will be some transverse motion when the electron reverses its direction towards the parent core. In contrast to an atom, a diatomic molecule is elongated along the molecular axis. Therefore, an electron close to one side of the nucleus could rescatter off an electron on the other side of the nucleus (~ 2.2 a.u. away for NO) in a CP field. This unique geometry of a diatomic molecule might enhance the rescattering cross section for CP leading to an NSDI component. However, it has been shown that the returning electron trajectory in a CP field is on the order of 50 a.u. away from the core [17], and this will lead to a vanishing possibility for the e-2e rescattering even for a large molecule. Therefore, rescattering does not play any significant role for the peculiar NSDI-like behavior in NO with CP. Furthermore, an accidental resonance for NO^{2+} with CP is also unlikely, since the LP counterpart does not show any peculiar enhancement at the same intensity range given that transitions are much more favorable for LP. (It can be seen in Fig. 4 that within the intensity range of $8\times 10^{13}-2\times 10^{14}$ W/cm^2, the flat ratio part of NO with CP is higher than those of N_2 and Ar, while NO with LP is over an order of magnitude lower than those in N_2 and Ar.) Finally, the fact that N_2 behaves like a structureless atom in ellipticity effects for both single and double ionization leads us to conclude that the peculiar behavior of NO is not simply a consequence of it being a molecule; instead, the different ellipticity behavior between N_2 and NO could be once again attributed to the difference in their electronic structures (N_2: closed shell; NO: closed shell plus one valence electron resembling the H atom), since the detailed electronic structure has been demonstrated to play key roles in influencing the strong-field excitation and ionization over a variety of strong-field phenomena [8–12].

To study further the possibilities of the influence of electronic structure on ellipticity effects, we consider an *ab initio* two-electron quantum mechanical calculation recently reported by us in investigating the dynamics of single and double strong-field ionization [11]. In this study, not only are the influences of the detailed electronic structure on nonsequential double ionization reinforced in these calculations, but the single-electron ionization is also demonstrated to be a

dynamic process correlated with the double ionization. In particular, we observed a decrease in the single ionization rate that occurs at exactly the same intensity when NSDI is most prominent. This indicates that single-electron ionization is suppressed when two-electron simultaneous emission becomes efficient. Therefore, it is natural for us to consider if there is any suppression in NO^+ with CP that could relate to the peculiar high NO^{2+} signal. However, due to the volume averaging in experimentally obtained signals, an ion yield will always monotonically increase with intensity even as the ionization rate starts to decrease [20]. Therefore, it will be impossible for us to observe experimentally a suppressed NO^+ ion signal even if it exits. As discussed above, it is reasonable to compare the single-ionization behavior of NO with the H atom because of the similarity in their valence electronic structure. *Ab initio* calculations are relatively easily accessible for the H atom due to its simplicity. We note a recent calculation reported in Ref. [17], where a suppressed ionization rate is seen in the H atom with CP for peak intensities higher than 0.02 a.u. Since the laser parameters and ionization potentials in our experiment ($\lambda = 800$ nm and $I_p = 9.25$ eV) are different from the H atom calculations ($\lambda = 526$ nm and $I_p = 13.6$ eV), we establish a comparison through scaling the ionization by the Keldysh parameter. The onset intensity of 0.02 a.u. for suppressed ionization in the H atom corresponds to a Keldysh parameter of $\gamma = 0.87$. The γ of 0.87 is transformed to an average intensity (note that peak intensity is used in Ref. [17]) of 1.0×10^{14} W/cm^2 in our experiment indicating that a suppression, if it exists, may occur at intensities above 1.0×10^{14} W/cm^2 in NO^+. This agrees with the intensity range for the observed enhancement in NO^{2+} in our experiments and therefore, it appears that the enhancement in NO^{2+} is somehow related to the suppression in NO^+. Further investigations are necessary to fully understand this peculiar ellipticity behavior in NO^{2+}.

In summary, we performed high-precision ion yield measurements and extend the study of ellipticity effects to molecular systems on both single and double ionization in strong laser fields. The closed-shell diatomic molecule N_2 behaves like the structureless rare-gas atom Ar in ellipticity effects following the prediction of the ADK model on both single and double ionization. The competing ionization efficiencies between LP and CP light, as predicted in the ADK model, is observed experimentally by studying the ion yields of N_2^+ versus NO^+. We further observe an anomalously high ion signal in NO^{2+} with CP at low intensities indicating an NSDI signature. While further investigations are necessary to fully understand this peculiar ellipticity behavior of NO^{2+}, we propose a hypothesis that a high ion yield of doubly ionized species can be due to the suppression of its singly ionized counterpart, and this hypothesis is supported through a connection between the experimentally observed enhancement in NO^{2+} and suppression in the H atom calculations, since NO has the same valence electronic structure as the H atom. If this is the case, electron structure is shown to play a crucial role in influencing the ellipticity dependence of strong-field ionization, in addition to a variety of other strong-field phenomena that have already been identified, such as single and double ionization, nonsequential ionization, charge asymmetric dissociation, molecular fragmentation, and strong-field dynamics [8–12]. The results presented in this paper demonstrate that the study of ellipticity effects is a rich field yet to be fully explored.

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