# Comparison Study of Atomic and Molecular Single Ionization in the Multiphoton Ionization Regime

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In this Letter, we report, for the first time in the multiphoton ionization regime, a comparison study of single-electron ionization of diatomic molecules versus rare gas atoms with virtually the same ionization potentials. In comparing $N_2^+$ to $Ar^+$, a higher ion signal is seen in $N_2^+$ compared to $Ar^+$ for linear polarization but the difference vanishes in circularly polarized light. In comparing $O_2^+$ to $Xe^+$, we observe a suppression in $O_2^+$ compared to $Xe^+$ for both linear and circular polarization but this suppression exhibits an intensity dependence; i.e., there is little suppression for $O_2^+$ at the lowest intensity range, but the suppression becomes increasingly stronger as the laser intensity increases. The multielectron screening model is used to discuss possible mechanisms of this intensity dependent suppression in $O_2^+$ in the multiphoton ionization regime.

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The understanding of photoionization processes is the foremost problem in strong-field atomic and molecular physics, since ionization always occurs when electrons in an atom or molecule are exposed to an ultrashort strong laser field that is comparable in strength to their Coulomb binding potentials. All the major problems studied in the current field, such as above-threshold ionization, high harmonic generation, molecular photodissociation, photoelectron spectroscopy, and few-cycle and attosecond pulse generation are derived directly or indirectly from electron ionization [1]. Following intensive study over the past two decades, most phenomena involving single-electron ionization in atoms have been relatively well understood [1]. However, there have been a number of observations suggesting that molecules in strong fields behave quite differently from what we have learned from atoms [2–4]. For example, in the tunneling regime, one would expect that different species have the same ionization strength if they have identical ionization potentials. Experimentally, however, a strong suppression has been seen in single-ionization yields in diatomic molecule $O_2$ compared to the rare gas atom Xe, although $O_2$ has virtually the same single-ionization potential as Xe (~12 eV) [2,3]. However, no suppression is seen in the diatomic molecule $N_2$ compared to its counterpart atom Ar, although $N_2$ and Ar also have virtually the same ionization potential of ~15.6 eV [3]. Subsequently, extensive efforts have been devoted to studying the single-ionization behaviors in diatomic molecules both experimentally and theoretically [2–9]. However, the physical mechanism of this fundamental problem still requires further investigation.

The comparison studies between atoms versus diatomic molecules have been mainly carried out in the tunneling ionization (TI) regime with near-IR Ti:sapphire femtosecond (fs) laser pulses [2–9]. No systematic comparison study has been performed in the multiphoton ionization (MPI) regime. Since single-electron ionization is probably the foremost problem in strong-field physics [1,5], it is of fundamental importance to extend this comparison study into the MPI regime. In this Letter, for the first time in the MPI regime, we perform such a comparison study of single-electron ionization in both $N_2$ versus Ar and $O_2$ versus Xe with 400 nm radiation. In comparing $N_2^+$ to $Ar^+$, a higher ion signal is seen in $N_2^+$ compared to $Ar^+$ for linear polarization (LP) but the difference vanishes for circular polarization (CP). In comparing $O_2^+$ to $Xe^+$, we again observe a suppression in $O_2^+$ compared to $Xe^+$ for both LP and CP but this suppression exhibits an intensity dependence; i.e., there is little suppression for $O_2^+$ at the lowest intensity range, but the suppression becomes increasingly stronger as the laser intensity increases, which leads the interaction towards the TI regime.

The laser used in our experiment is a Ti:sapphire laser system consisting of a mode locked oscillator and a two-stage amplifier (a regenerative amplifier and a two-pass external amplifier) running at a 1 kHz repetition rate, producing pulses of energy about 1.2 mJ/pulse with a central wavelength of 800 nm. A type-I cut BBO crystal is used to generate second harmonic pulses estimated about 130 fs in duration at 400 nm. The polarization of the incident 800-nm light is perpendicular to the optical table so that the polarization of the generated 400-nm pulses is parallel to the optical table. After having the 400-nm pulses reflecting off a number of dichroic mirrors (high reflection at 400 nm and high transmission at 800 nm), only pulses at 400 nm are focused into the target chamber with a thin lens. A quarter-wave plate at 400 nm is placed before the lens to obtain either LP or CP. The chamber base pressure is $<5.0 \times 10^{-10}$ Torr. The details of our experimental setup have been described elsewhere [9,10]. In brief, a standard time-of-flight (TOF) mass spectrometer is used for ion collection and detection. At the end of the TOF, ions are detected with a microchannel plate as a function of flight time. This signal is further amplified, discriminated, and either integrated with a boxcar to produce ion yields or sent to a multihit time digitizer to generate TOF mass

 

spectra. To minimize the effects of pulse-to-pulse energy fluctuation, in our experiment, the pulse energy of each laser shot is monitored and assigned to its instantaneous intensity. Eventually, each data point at a given intensity in the ion yield plots is obtained by averaging over $10^4$ to $3 \times 10^6$ laser shots at this intensity to ensure a sufficiently high statistical accuracy. The time digitizer used provides an ultrahigh flight time resolution of 100 ps. The TOF axis is parallel to the optical table, and therefore the linear polarization of the 400-nm field is also oriented parallel to the TOF axis. The TOF voltage plates for extracting and accelerating ions each has only a 1-mm pinhole allowing ions to pass through. High-precision ionization yield measurements of different atomic and molecular species are essential in order to compare different channels. Using a technique described in Ref. [10], we are able to accurately determine the flight time and width of a certain species and isolate it from contamination from adjacent peaks.

The MPI regime can be distinguished from the TI regime according to the adiabatic Keldysh parameter $\gamma = (I_p/2U_p)^{1/2}$ [11], where $I_p$ and $U_p$ are the ionization potential and the ponderomotive energy, respectively. If $\gamma$ is less than 1, the ionization will be dominated by the tunneling process; if $\gamma$ is larger than 1, multiphoton ionization will play a more dominant role. In our experiment, the peak intensity of the generated second harmonic pulses at 400 nm is less than $5 \times 10^{13}$ W/cm$^2$, and for all the atomic and molecular species studied here, the Keldysh parameter $\gamma$ is determined to be always greater than 2.9. Therefore, our experiment at 400 nm is predominately carried out in the MPI regime, in contrast to most of the previous studies at 800 nm in the TI regime [2–9].

Ion yields of singly ionized $N_2$ versus Ar and $O_2$ versus Xe using both linearly and circularly polarized light are plotted in Figs. 1 and 2. Our experimental results in the MPI regime are quite different from the previous studies in the TI regime [3,4]. Previous studies in the TI regime have shown that $N_2^+$ and $Ar^+$ have very similar ionization strength. As we can see here from Fig. 1, ion yield of $N_2^+$ is much higher than $Ar^+$ with LP. Since our experiment is performed in the MPI regime, and this discrepancy has to be attributed to phenomena that are relevant in the MPI regime, e.g., resonance-enhanced MPI [12,13] and above-threshold ionization [1]. Resonance-enhanced MPI occurs when an intermediate state that resides $m$ laser photon energy above the ground state. In this case, an atom or molecule is first excited to the intermediate state with a rate of $W_m$, and then further ionized to the continuum by absorbing $n$ additional photons with a rate of $W_n$. In most cases, this intermediate state is very close to the ionization threshold and thus, $W_m$ is smaller than $W_n$. Therefore, the total ionization rate of the resonance-enhanced MPI, $W_{\text{ionize}}$, is mainly governed by the first multiphoton resonant step ($W_{\text{ionize}} \approx W_m$) and the total ionization rate is usually much larger than a nonresonance MPI [12,13]. The single-ionization potential of $N_2$ and Ar is ~15.6 eV, and at least 6 photons at 400 nm are required to reach their ionization thresholds when the ac Stark shift of the ionization potential is considered. The intensity dependent ion yield of $N_2^+$ in Fig. 1 is fitted with linear regression, and we obtain a slope of about 5.3 before saturation. This intensity dependence indicates that a resonance-enhanced MPI process with $m = 5$ and $n = 1$, hereby labeled as (5 + 1), plays an important role in forming $N_2^+$. Similarly, other resonant enhanced MPI, such as (2 + 1) and (3 + 1) processes, have been seen in $N_2^+$ using other wavelength radiation [14–16]. Indeed, plenty of Rydberg states are in the 5-photon resonance range from the ground state of $N_2$, $X^1\Sigma_g^+$, and some possible resonance states are $c'^1\Sigma_u^+$, and $c^1\Pi_u$ [17]. Similar to the observation in the TI regime [3], however, $N_2^+$ and $Ar^+$ show very similar intensity dependence when CP is used. This confirms that the enhanced $N_2^+$ LP yield is due to the multiphoton resonance enhancement because the intermediate states for resonance ionization will be strongly restricted by the large angular momentum with CP [18]. As a result, by turning off resonance using CP, $N_2^+$ shows virtually the same intensity dependence as $Ar^+$ since the two species have nearly the same single-ionization potential.

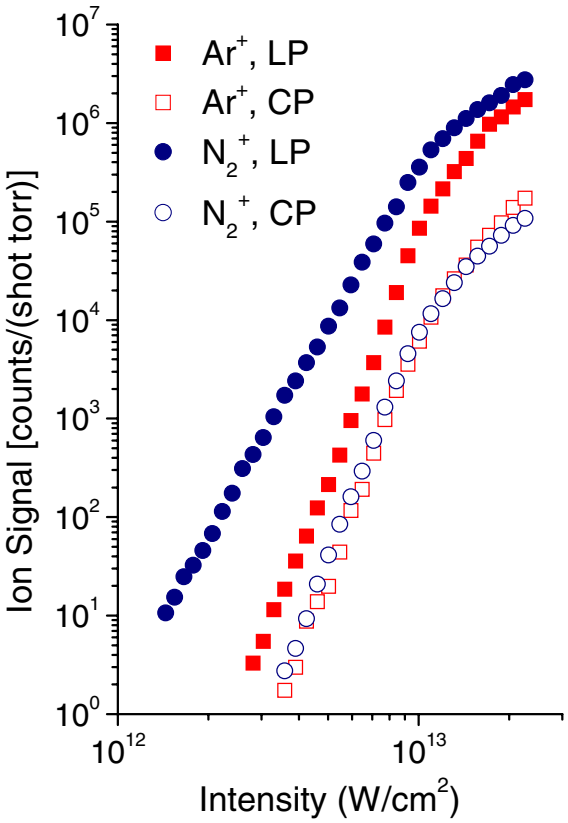


FIG. 1 (color online). Single-ionization yields for $N_2$ and Ar using LP and CP light at 400 nm.

Because of much simpler electronic states in rare gas atom Ar compared to the molecule $N_2$, it is not surprising that the resonance-enhanced MPI is not observed in $Ar^+$.

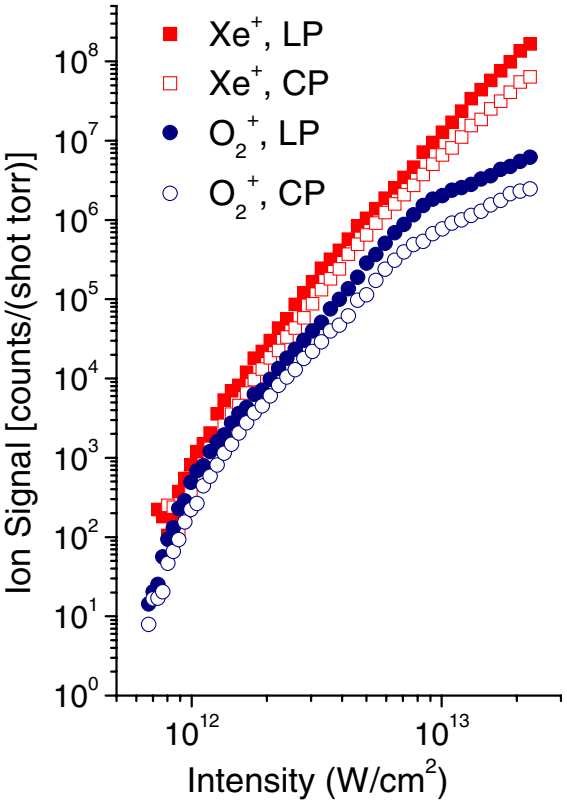


FIG. 2 (color online). Single-ionization yields for $O_2$ and Xe using LP and CP light at 400 nm.

The slope of the intensity dependent $Ar^+$ for LP obtained by linear fit is about 7.9 before saturation. As discussed in Ref. [19], this intensity dependence indicates that an 8-photon process including a 2-photon above-threshold transition plays an important role in obtaining $Ar^+$ in our experiment. With circularly polarized light, $Ar^+$ and $N_2^+$ have similar ion yields with an intensity dependent slope of about 7.7, suggesting that an 8-photon process including a 2-photon above-threshold transition plays an important role in both $Ar^+$ and $N_2^+$ with CP when the resonance-enhanced MPI is turned off by CP in our experiment [1,19]. Note, our experiment is performed with randomly oriented molecules. Although molecular alignment may play an important role in the tunneling regime for multiple electron dissociative ionization, using randomly oriented molecules has little effect on our experimental results since our experiment here studies single-electron ionization in the multiphoton regime.

As mentioned earlier, previous studies on $O_2^+$ versus $Xe^+$ [2–4] in the TI regime by using 800-nm ultrashort laser pulses revealed that the ion yield of $O_2^+$ is substantially lower than $Xe^+$, although the two species have virtually the same ionization potentials. In the MPI regime at 400 nm, we can see from Fig. 2 that the difference between the $O_2^+$ and $Xe^+$ ion yields is quite small at the lowest intensity range, but suppression appears in the $O_2^+$ ion yields compared to $Xe^+$ for both LP and CP as intensity increases. The difference between $Xe^+$ and $O_2^+$ reaches the maximum at the highest intensity. Therefore, we see a clear intensity dependent suppression in $O_2^+$ compared to $Xe^+$ in the MPI regime. Note, our data in Figs. 1 and 2 have taken into account the pressure correction due to the vacuum gauge sensitivity on different type of gases. The sensitivity of the multichannel ion detector on different gases was not always included in data correction in previous 800-nm experiments in the TI regime [3,4]. We choose here not to include this possible correction from the multichannel ion detector efficiency. However, such a correction (proportional to $Z/M^{1/2}$, with $Z$ is the charge and $M$ is the mass of the ion [3]), if included, will further suppress $O_2^+$ compared to $Xe^+$ in our data.

It is natural to think that the similar ionization strength of $O_2^+$ compared to $Xe^+$ at the lowest intensity may be also due to the resonance-enhanced MPI in $O_2^+$ similar to $N_2^+$. However, similar ionization behavior is seen in both LP and CP data, indicating that the resonance-enhanced MPI does not play a key role since CP should substantially reduce the resonance enhancement. Among various theoretical studies that try to explain the suppressed ionization in $O_2^+$, three models [5–7] have exhibited some success, and all the three models are based on the original concept proposed in Ref. [3] that the detailed electronic structures play a key role in molecular ionization. Muth-Bohm *et al.* [6] attributed the suppressed $O_2^+$ to a destructive interference between the waves of two ionizing electrons from the two atomic centers due to the antisymmetric distribution of the outermost electrons. Alternatively, Tong *et al.* [7] derived a molecular Ammosov-Delone-Krainov (ADK) model with modified structural parameters that allow their model to fit the suppressed ion yields in $O_2^+$. In contrast to the above two models involving more theoretical efforts, Guo suggested a very intuitive model [5] that can quantitatively account for the suppression in $O_2^+$ by taking into account subtle but significant multielectron effects. These three models, however, were mainly developed in the TI regime by studying $O_2^+$ at 800-nm light [5–7], and it will be highly desirable to have a theoretical framework that can guide us to understand the experimental results in the MPI regime in this Letter. Since such a theoretical work is absent, we will try to discuss the relevance of these three models to our data here. First of all, the molecular ADK model was specifically developed in the TI regime [7] and therefore, it does not apply to this experimental study in the MPI regime. The wave function interference model shows that the suppression of $O_2^+$ is nearly independent on laser intensity with near-IR light [6]. Since the effects of intensity and wavelength are not perceivable from this model without involving further calculations, we will refrain from further discussion of this model. In contrast to the above two models, the multielectron screening model [5] provides a very intuitive way to understand different effects in single ionization, and we will try to relate our experimental results here in the framework of this model.

Molecule $O_2$ has an open-shell electronic structure and the two outermost valence electrons occupy two degenerate $1\pi_g$ sublevels, and therefore, the spatial wave function of the two outermost electrons is antisymmetrically distributed around the core [5]. Pictorially speaking, based on the multielectron screening model, as one of the outer electrons is liberated and moving away from the ion core, the time that takes the other electron to effectively screen the receding electron determines the degree of the suppression in $O_2^+$ [5]. The multielectron screening model is developed in the TI regime and thus, we expect to see a stronger suppression in $O_2^+$ with a higher tunneling component (smaller $\gamma$ value) if the interaction is not in the pure TI regime [5]. Furthermore, the multielectron screening model predicts that the suppression in $O_2^+$ should be stronger when the ionized electron is removed from the ion core faster [5]. In our experiment, the adiabatic Keldysh parameter $\gamma$ decreases as intensity increases and therefore we are moving towards the TI regime as the intensity increases. Since there is no absolutely clear boundary between the MPI and TI regimes and, in many cases, phenomena in the MPI regime can be successfully explained by the TI theories [20], we can consider that the TI component in our experiment will become increasingly higher as the intensity increases, which leads to a stronger suppression in $O_2^+$ at higher intensities. Furthermore, as the laser intensity increases, the sudden removal of the first electron may become more and more pronounced, and this will also lead to a greater degree of suppression in $O_2^+$ based on the multielectron screening model [5]. Therefore, the multielectron screening model may qualitatively suggest the trend of the intensity dependence in the suppressed $O_2^+$ at 400 nm. However, more rigorous theoretical studies are required for us to further understand the behaviors of atomic and molecular ionization in the MPI regime. The experimental results presented in this Letter provide a direction for further experimental and theoretical work in comparing single ionization of atoms and molecules in the MPI regime.

In summary, we perform, for the first time in the MPI regime, a comparison study of single-electron ionization of diatomic molecules and their counterpart rare gas atoms at 400 nm. In comparing $N_2^+$ to $Ar^+$, a higher ion signal is seen in $N_2^+$ compared to $Ar^+$ for linear polarization but the difference vanishes in circularly polarized light. Resonance-enhanced MPI is believed to play a role in the enhanced $N_2^+$ yield with LP. In comparing $O_2^+$ to $Xe^+$, we observe a suppression in $O_2^+$ compared to $Xe^+$ for both LP and CP but this suppression exhibits an intensity dependence, i.e., there is little suppression for $O_2^+$ at the lowest intensity range, but the suppression becomes increasingly stronger as the laser intensity increases, which leads the interaction towards the TI regime. The multielectron screening model is used to discuss possible mechanisms of this intensity dependent suppression in $O_2^+$ in the MPI regime. Our experimental results presented in this Letter extend the comparison study of atomic and molecular ionization into the MPI regime and provide initial steps for future experimental and theoretical studies in this direction.

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