Rydberg excitation of neutral nitric oxide molecules in strong UV and near-IR laser fields*

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Rydberg state excitations of neutral nitric oxide molecules are studied in strong ultraviolet (UV) and near-infra-red (IR) laser fields using a linear time-of-flight (TOF) mass spectrometer with the pulsed electronic field ionization method. The yield of Rydberg molecules is measured as a function of laser intensity and ellipticity, and the results in UV laser fields are compared with those in near-IR laser fields. The present study provides the first experimental evidence of neutral Rydberg molecules surviving in a strong laser field. The results indicate that a rescattering-after-tunneling process is the main contribution to the formation of Rydberg molecules in strong near-IR laser fields, while multi-photon excitation may play an important role in the strong UV laser fields.

Keywords: strong laser fields, neutral Rydberg excitation, nitric oxide

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1. Introduction

The interactions of atoms and molecules with strong laser fields have been the subject of many theoretical and experimental studies during the last three decades. The celebrated three-step rescattering model, which was proposed first by Corkum in 1993[1] has been widely viewed as the underlying mechanism of many strong-field atomic phenomena in the tunneling ionization (TI) regime.[2,3] According to this model, an electron in an atom is liberated through tunneling ionization, then is accelerated in the laser field, and finally can revisit the parent ion upon reversal of the directional vector of the laser field, resulting in an interesting rescattering-after-tunneling process, for example, above-threshold ionization (ATI),[4] high-harmonic generation (HHG),[5] and non-sequential double ionization (NSDI).[6]

Recently, Nubbemeyer *et al.*[7] measured a substantial fraction of neutral excited He atoms (He^*) surviving in a strong 30 fs and 800-nm laser field in the TI regime. The formation of He^* is attributed to the capture of the tunneling electron into the Rydberg state under the combined interaction of the Coulomb field and laser field. The authors refer to the process as frustrated tunneling ionization (FTI), and it indicates that the FTI completes the rescattering-after-tunneling process. Since then, many experimental and theoretical studies have been carried out on FTI of atoms in strong laser fields, for example, acceleration of neutral atom,[8,9] low-energy photon electron yield maximum for dimers,[10] as well as excited atoms from fragmentation of diatomic molecules such as H_2,[11] D_2,[12] N_2,[13] and Ar dimer.[14]

On the other hand, in their numerical calculation on the silver atom, Popov *et al.*[15] proposed an alternative explanation for the neutral Rydberg excitation in a strong laser field. They indicated that the excitation of neutral atoms is caused by multi-photon resonance between the ground state and a group of Rydberg states, via the interference stabilization (IS)[16] or Kramers–Henneberger (KH) stabilization.[17] Indeed, the population trapping in a strong laser field was observed in the multiphoton ionization (MPI) regime about 30 years ago.[18,19] The excited states populated in the femtosecond laser field usually have a large angular momentum quantum number l;[14,20] therefore they are incapable of absorbing another photon, thereby becoming ionized.[21]

For molecules, the neutral Rydbergs produced in a strong laser field have not been studied. High Rydberg states of molecules exhibit unique properties that have aroused the intense interest in high resolution spectroscopy, molecular collisions, chemical dynamics, etc.[22] As a new physical process is driven by a strong laser field, Rydberg state excitation is expected to be used for accelerating neutral atoms, which may lead to new applications in both fundamental and applied physics.[8] To date, almost all the previous studies have focused on the Rydberg excitation of atoms in near-IR strong laser fields, in which both TI and MPI contribute to the strong-field processes. As is well known, the strong-field processes in UV laser fields are mainly in the MPI regime, particularly for atoms or molecules with low ionization potential (I_P). It is

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worthwhile to extend the investigation of the Rydbergs excitation to the strong UV laser fields, and comparing it with the Rydbergs excitation in the near-IR laser fields can shed light on the underlying mechanism of neutral Rydberg excitation.

In this work, we carry out experimental studies on Rydberg excitation of NO molecules in 800-nm and 400-nm laser fields separately. The NO molecule has a relatively low I_p (9.264 eV), and has closed-shell structure plus one $\pi_g 2p$ valence electron resembling the electronic structure of the hydrogen H atom (the so-called "hydrogen-like molecule"[23]). Using the pulsed electronic field ionization method, we observe the neutral NO Rydberg excitations in near-IR and UV strong laser fields. To the best of our knowledge, this is the first experimental evidence that neutral excited molecules survive in strong laser fields. We measure the yield of Rydberg molecule as a function of laser intensity and ellipticity, and compare the results in 800-nm laser fields with those in 400-nm laser fields. Different mechanisms of forming the neutral molecular Rydbergs are discussed based on the experimental results.

2. Experiment setup

The experimental setup used for femtosecond laser ionization experiments is similar to that described in our previous studies.[24,25] The NO molecules are introduced into the vacuum chamber through a leak nozzle with an aperture of 10 μm. The base pressure of the interaction chamber is 2×10^{-6} Pa and the operating pressure is about 3×10^{-4} Pa. The laser used in the experiment is a Ti:sapphire system running at a 1-kHz repetition rate, producing over 4 mJ/pulse in 50-fs pulses with a central wavelength of 800 nm. The 400-nm pulses are produced by frequency doubling the 800-nm pulse using a BBO crystal. A half-wave plate and a Glan prism are inserted into the laser beam to vary the laser intensity continuously. The polarization of the laser pulse is controlled by rotating a quarter-wave plate before it is focused to the vacuum chamber. The peak intensity of the laser field is calibrated by comparing the measured saturation intensity of Xe^+ with that calculated by the Ammosov–Delome–Krainov (ADK) model.[26]

A linear time-of-flight (TOF) mass spectrometer is used to detect the produced cations from strong-field ionization. In order to detect the neutral molecular Rydbergs, the direct ionized ions (NO^+) are first pushed away from the detector by an electric field, the remaining high-lying neutral Rydbergs (NO^*) are then ionized by another electric field with a typical delay time of 1.0 μs. The ions from field-ionization of Rydbergs, $(NO^*)^+$ are detected by dual micro-channel-plates at the end of flying about 50 cm. The mass-resolved ion signals are recorded using a digital oscilloscope (Tektronix TDS 3054B) and sent to a PC for analysis. All experimental data are normally averaged over 10^3 laser shots.

3. Results and discussion

Because of a variety of decay processes in molecular Rydbergs, particularly those with mid- or low-principle number, the lifetime is so short that the molecular Rydbergs are unlikely to survive in the free-flight time (typically hundreds of microseconds for a molecular beam). In other words, neutral molecular Rydbergs cannot be directly measured as done in Nubbemeyer's paper.[7] On the other hand, the mass-resolved pulse field ionization method is feasible to investigate the neutral Rydberg excitation in a strong laser field. Typical ToF mass spectra of pulse-field ionization of neutral Rydbergs ($(NO^*)^+$) and direct ionization (NO^+) are shown in Fig. 1, recorded by linearly polarized 400-nm or 800-nm strong laser field with an intensity of 1×10^{14} W·cm^{-2}. The fight time of $(NO^*)^+$ is 1 μs larger than that of NO^+, which is exactly consistent with the delay of the pulsed electronic field, indicating the neutral molecular Rydbergs surviving in both near IR and UV strong laser fields.

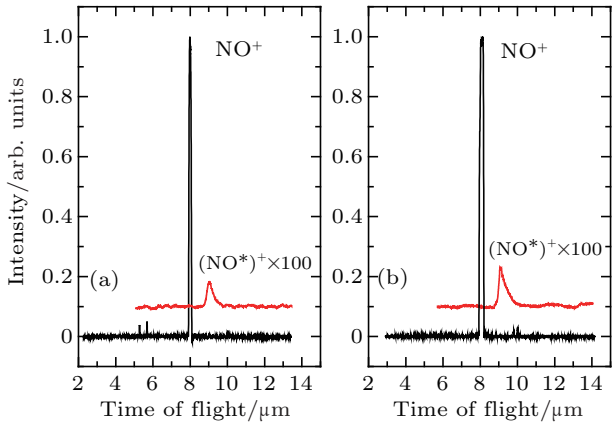


Fig. 1. (color online) Typical ToF mass spectra of neutral Rydberg $(NO^*)^+$ and ionized NO^+, recorded at 400 nm (a) and 800 nm (b) with an intensity of 1×10^{14} W·cm^2.

For atomic Rydberg excitation in strong 800-nm laser field, Nubbemeyer *et al.*[7] suggested that the underlying mechanism be a rescattering-after-tunneling process. In the case of strong UV field such a process is expected to be greatly suppressed, owing to the reduced probability of rescattering with the ionic core by increasing the frequency of the laser field. However, the results in Fig. 1 show that the yield of $(NO^*)^+$ in the 400-nm laser field is actually comparable to that in the 800-nm laser field, indicating that the rescattering-after-tunneling process is not a main contribution to the formation of neutral molecular Rydbergs in a strong UV laser field.

In order to shed light on the mechanism of neutral molecular Rydberg excitation in a strong laser field, we investigate the $(NO^*)^+$ yield as a function of laser intensity and ellipticity, and compare the results in a 400-nm strong laser field with those in an 800-nm strong laser field. Figure 2 shows the dependences of the $(NO^*)^+$ yield on the peak intensity of the linearly polarized strong laser pulse with central wavelengths

being 400 nm (Fig. 2(a)) and 800 nm (Fig. 2(b)). For comparison, the results of NO^+ are also presented in the figures. For either of the wavelengths, the yield of Rydberg excitation first increases as the laser intensity increases, and then is saturated at approximately the same intensity as the intensity at which the ionization takes places for 400-nm and 800-nm strong laser fields, respectively.

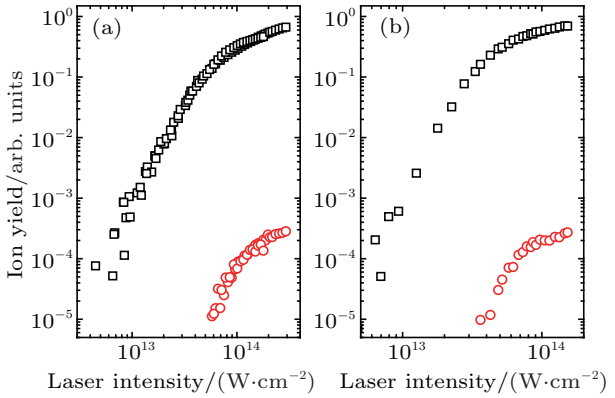


Fig. 2. (color online) Dependences of the ion yield of NO^+ (black square) and $(NO^*)^+$ (red circle) on the peak intensity of the linearly polarized strong laser pulse, with central wavelengths being 400 nm (a) and 800 nm (b).

In the strong laser field ionization, the multiphoton ionization (MPI) will be dominant if the adiabatic Keldysh parameter $\gamma > 1$, while $\gamma < 1$, the ionization is in tunneling ionization (TI) regime ($\gamma = (I_p/2U_p)^{1/2}$,[27] where I_p and U_p are the ionization potential and the ponderomotive energy). In our experiments, the adiabatic Keldysh parameter for the detection of the Rydberg ions $(NO^*)^+$ is between 1.6 and 0.6 for the 800-nm laser, and it is between 2.5 and 1.02 for the 400-nm laser. Although the boundary ($\gamma = 1$) between MPI regime and TI regime is not so strict, it is expected that the MPI plays a more important role in the 400-nm laser field than in the 800-nm laser field. The global fittings of the log–log curves of the NO^+ signal versus laser intensity at low intensities of the 400-nm laser field result in a slope of roughly 3.1, very close to the minimal number of photons that need to be absorbed to allow the multi-photon ionization of an NO molecule ($I_p = 9.264$ eV). This suggests that the neutral NO Rydbergs surviving in a strong 400-nm laser field may be formed in the MPI regime instead of the TI regime.

It is widely accepted that the Rydberg excitation of atoms in TI regime is a rescattering-after-tunneling process. The direct experimental evidence of such a process is the strong dependence of the neutral He^* yield on the laser ellipticity,[7] which is in excellent agreement with the Monte Carlo simulation result based on a semi-classical model.[28] This is a general behavior that is expected by the three-step rescattering model,[1] as also shown in HHG[29] or NSDI.[30] In order to further demonstrate the different mechanisms in the formation of neutral molecular Rydbergs in strong UV and near-IR laser fields, we measure the $(NO^*)^+$ yield as a function of laser ellipticity. The results are shown in Fig. 3. For either 400 nm or 800 nm, the experimental data are normalized to the maximum. The laser peak intensity is kept at constant values of 9×10^{13} W·cm^{-2} for 400 nm and 8×10^{13} W·cm^{-2} for 800 nm, with which the total ionization rates of NO for different wavelengths are equal in the case of linear polarization.

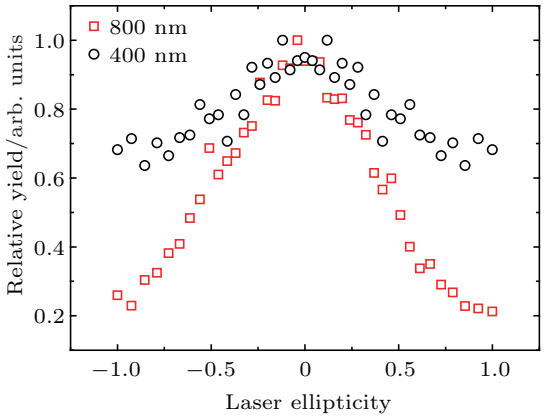


Fig. 3. (color online) Dependences of Rydberg $(NO^*)^+$ yield on laser ellipticity, with the central wavelengths being 400 nm (black circle) and 800 nm (red square).

It can be seen from Fig. 3 that in the 800-nm laser field, the yield of $(NO^*)^+$ decreases significantly as the laser ellipticity is increased. This is consistent with the prediction of the rescattering-after-tunneling scenario, that is, with increasing the ellipticity of laser polarization, recollision with the parent ions diminishes due to the greater drift momentum spread of the returning electron wavepacket. In neutral He atoms, the He^* yield in the 800-nm laser field is completely suppressed when the laser ellipticity is larger than 0.3.[7] By Gaussian fitting our experimental data, the half width at half maximum of the $(NO^*)^+$ yield versus ellipticity is evaluated to be $\sigma_\varepsilon = 0.49$, indicating much weaker elliptical dependence than that in the case of He^*. This could be attributed to much lower I_P of NO ($I_P = 9.26$ eV) than that of He ($I_P = 24.59$ eV). As predicted in a recent three-dimensional semi-classical calculation,[31] the width of the survival window (i.e., σ_ε) varies with atomic ionization potential; the lower I_P results in much larger survival window of neutral atomic Rydberg excitation. In their calculation, the σ_ε value of Be atoms ($I_P = 9.32$ eV, comparable to that of NO) is estimated to be $\sim$0.44,[31] which is close to that of NO molecules observed in this study. One can see that the $(NO^*)^+$ signal does not completely disappear in the circularly polarized 800-nm laser field (ellipticity = 1), which contradicts the prediction of the three-step rescattering model. The underlying mechanism of the broad survival window in Rydberg excitation in strong laser fields is still unclear, which may exhibit chaotic scattering as

indicated in Ref. [27]. Further experimental and theoretical studies are necessary to address such an issue.

On the other hand, the elliptical dependence of $(NO^*)^+$ in the 400-nm laser field is quite different from in the 800-nm laser field. The $(NO^*)^+$ yield only slightly decreases as the laser ellipticity is increased. The $(NO^*)^+$ yield under circular polarization (CP) is as high as $\sim 70\%$ of that under linear polarization (LP). Unlike the results in the 800-nm laser field, the elliptical dependence of the Rydberg excitation in the 400-nm laser field is irrelevant to the ionization potential and atom/molecule species. In our study, we observe exactly the same elliptical dependence of $(Xe^*)^+$ (I_P (Xe) = 12.13 eV) as that of $(NO^*)^+$. It is indicated that rescattering-after-tunneling is not a dominant process in Rydberg excitation in a strong UV laser field.

As mentioned above, the neutral NO Rydbergs may be formed in the MPI regime in the strong 400-nm laser field. Multi-photon resonance between the ground state and a group of excited (Rydberg) states should contribute to Rydberg excitation in the strong UV laser field. Because the Rydberg states observed in this study have high principal quantum numbers larger than 20, the energy interval of the adjacent Rydberg states is less than the laser bandwidth and the probability of multi-photon resonance strongly depends only on the laser intensity instead of on laser ellipticity. Since in Fig. 3 the peak intensity is kept at a constant value for different laser ellipticities, the slight decrease of the $(NO^*)^+$ yield may be due to different electric field intensities (the electric field intensity in CP laser pulse is $1/\sqrt{2}$ of that in LP laser). Figure 4 shows the ratio of the $(NO^*)^+$ yield in CP laser fields to that in LP laser fields as a function of laser peak intensity. It can be seen that in the intensity range under study, the ratio in the 400-nm laser field is around 0.7, about 3–4 times larger than that in the 800-nm laser field. This indicates that the mechanism of Rydberg excitation in UV laser field does not change in the investigated laser intensity range.

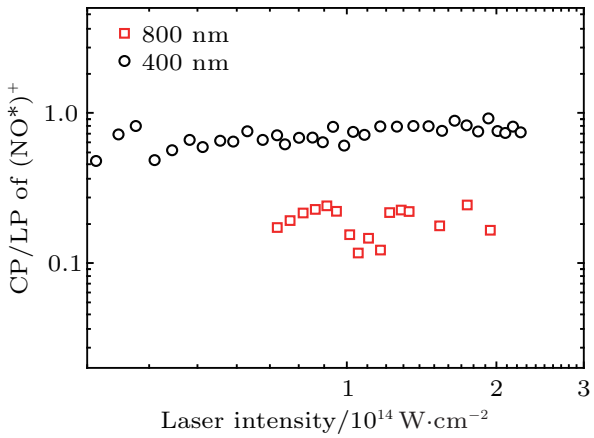


Fig. 4. (color online) Plots of ratio of $(NO^*)^+$ yield between CP and LP versus laser intensity with the central wavelengths being 400 nm (black circle) and 800 nm (red square).

4. Conclusions

In this paper, we show the first experimental evidence of the neutral excited molecule NO surviving in a strong femtosecond laser field. The dependences of $(NO^*)^+$ yield on laser intensity and ellipticity are measured in 400-nm and 800-nm laser fields. It is indicated that rescattering-after-tunneling is a main contribution to the production of $(NO^*)^+$ in the strong 800-nm laser fields, while multi-photon resonance between ground state and a group of Rydberg states may be dominant in the formation of excited molecules in the strong UV laser fields.

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