PHYSICAL REVIEW A **71**, 021405(R) (2005)

Observation of selective charge separation following strong-field single ionization

Chunlei Guo*
The Institute of Optics, University of Rochester, Rochester, New York 14627, USA

(Received 16 September 2004; published 28 February 2005)

In this paper, we report on an apparently anomalous observation in the dissociation channels of singly ionized nitric oxide (NO) molecules. We observe that the NO molecules, when oriented perpendicular to the laser polarization, appear to preferentially dissociate into the $N^+ + O$ channel rather than the $N + O^+$ channel, despite the fact that the latter channel is more energetically favorable. A careful examination of the unique electronic structure of the NO molecule suggests that this observation is most likely due to the influence of the detailed electronic structure of NO on its strong-field ionization dynamics, which leads NO^+ created in strong fields to dissociate differently from that in weak fields. This study reinforces our understanding of the fundamental differences between ionization dynamics in strong fields versus weak fields.

DOI: 10.1103/PhysRevA.71.021405 PACS number(s): 42.50.Hz, 33.80.Rv, 33.80.Wz

The understanding of the photoionization processes is of critical importance in strong field atomic and molecular physics since nearly all the major strong-field domains, such as above-threshold ionization, high harmonic generation, molecular photodissociation, and photoelectron spectroscopy, are derived directly or indirectly from electron ionization [1–3]. Following extensive prior studies, most aspects of single-electron strong-field phenomena in rare gas atoms have been relatively well understood [1,2]. However, single-electron strong-field ionization in molecules has encountered difficulties and continues to challenge our current understanding in strong-field physics [4–7]. One of the well-known examples reflecting the complexity of molecules is the observation that the single ionization yield of O_2 is substantially lower than that of the rare gas atom Xe, although O_2 has virtually the same ionization potential as Xe ($\sim$12 eV) [4,5]. At first glance, the anomalous behavior of O_2 may be because O_2 is a molecule and is different from the rare gas atom Xe. However, our further experiment also shows that the low ion signal is not observed in N_2, i.e., N_2 behaves like the rare gas atom Ar that has the same single-ionization potential as N_2 ($\sim$15.6 eV) [5]. This indicates that the peculiar behavior of O_2 is not a simple consequence of its being a molecule. Rather, the fact that N_2 behaves like a structureless atom, while O_2 shows distinct nonatomiclike behavior, indicates that subtle details of the electronic structure play a key role in influencing strong-field excitation and ionization, since N_2 has a closed-shell electronic structure, while the outermost orbital $(1\pi_g)^2$ of the ground state of O_2 is only half filled [5–7].

Most of the previous work in studying atomiclike and nonatomiclike behaviors of molecules has focused on single electron ionization [4–7]. In this paper, we extend the study to the subsequent single-ionization induced dissociation channels in molecules. Here, we report on an apparently anomalous selective charge separation in the dissociation channels following the single ionization of a heteronuclear diatomic molecule, nitric oxide (NO). Similar to the O_2 experiments [5,6], our observation in NO appears to deviate dramatically from what would be expected based on energy level consideration.

The laser used in the experiment is an amplified Ti:saphire system consisting of a mode-locked oscillator and a two-stage amplifier (a regenerative amplifier and a two-pass external amplifier). After final pulse compression, the system generates 55-fs pulses of about 1.5 mJ/pulse at a 1-kHz repetition rate with the central wavelength at 800 nm. A half-wave plate and a polarizer assembly is used to vary the pulse energy. The beam is weakly focused, using a lens of $f=30$ cm, to a near diffraction-limited spot size of about 40 μm in the center of the extraction region of a time-of-flight (TOF) mass spectrometer. The Raleigh range of the focused beam is about 3 mm. The chamber base pressure is less than 5×10^{-10} torr. The pulses are negatively chirped at the output of the amplifier to precompensate for the dispersion of all the optics prior to interacting with the gas media inside the chamber. The TOF is similar to that described in Refs. [5,8]. 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. The time digitizer used (ORTEC model 9353) has an ultrahigh flight time resolution of 100 ps. To minimize the signal average effects associated with the focused laser intensity distribution, the TOF voltage plate for ion extraction has only a 1-mm pinhole opening, similar to that described in Refs. [5,8]. An ion-ion correlation technique is used to deduce the identity of different dissociation channels [8].

Three chemical pathways exist following single electron ionization of NO: one ionic channel (NO^+) and two dissociation channels ($N^+ + O$ and $N + O^+$), illustrated as follows:

$$\begin{aligned} NO &\rightarrow NO^+ + e \quad \text{molecular ionic channel} \\ &\rightarrow N^+ + O + e \quad \text{dissociation channel; labeled as N(1,0)} \\ &\rightarrow N + O^+ + e \quad \text{dissociation channel; labeled as O(1,0)}. \end{aligned}$$

Note, throughout this paper, we label channel $N^+ + O$ as N(1,0), and channel $N + O^+$ as O(1,0). The energy thresholds

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*Electronic address: guo@optics.rochester.edu

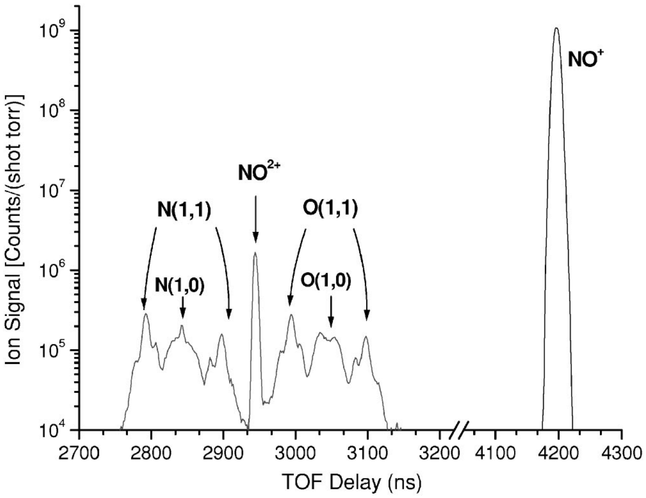

FIG. 1. TOF data show NO$^+$, N$^+$, and O$^+$ in a linearly polarized field at an intensity of 5×10^{14} W/cm^2. N(1,1) and O(1,1) denote the N$^+$ and O$^+$ signals, respectively, from the N$^+$+O$^+$ channel.

for the NO$^+$, N(1,0), and O(1,0) channels are about 9, 20.2, and 21.2 eV above the ground state of NO molecule [9]. Therefore, it is much easier to obtain the ionic channel, NO$^+$, than the dissociation channels, N(1,0) and O(1,0). This can be understood from both experimental results and electronic structure analysis, as explained below.

Experimentally, Fig. 1 shows that NO$^+$ yield is higher than the dissociation channels by a factor of nearly 10^4, indicating that the molecular ionic channel dominates the end product following single ionization of NO. This observation can be also understood based on the electronic structure analysis of NO as follows. The so-called "hydrogenlike molecule," NO is well known for having an electronic structure resembling that of the hydrogen atom. The outer electronic configuration in NO, $(1\pi)^4(5\sigma)^2(2\pi)^1$, consists of closed-shell orbitals $(1\pi)^4$ and $(5\sigma)^2$ plus one outermost 2π electron [9]. Both $(5\sigma)^2$ and $(2\pi)^1$ are antibonding orbitals, while $(1\pi)^4$ is a bonding orbital [9]. The three different channels following the singly ionized NO correspond to the removal of different electrons in NO. If we remove the outermost electron from the antibonding orbital 2π or even one of the antibonding 5σ electrons, the remaining bonding electrons should leave the singly ionized NO in the ionic state NO$^+$. If we remove an electron from the inner-shell 1π-bonding orbital, dissociation can occur and one of the two dissociation channels should be the end product depending on the exact electron removed. Pictorially speaking, if we remove an electron closer to N, the N(1,0) channel should be more likely to result; if we remove an electron closer to O, the O(1,0) channel should be more likely to result. From this analysis, we can see that ionic channel NO$^+$ is clearly much more energetically favorable than the dissociation channels since it involves removing the outmost least-bound antibonding 2π electron. This analysis is clearly consistent with the experimental observation that the NO$^+$ signal is nearly four orders of magnitude higher than the dissociation channels, N(1,0) and O(1,0) (Fig. 1).

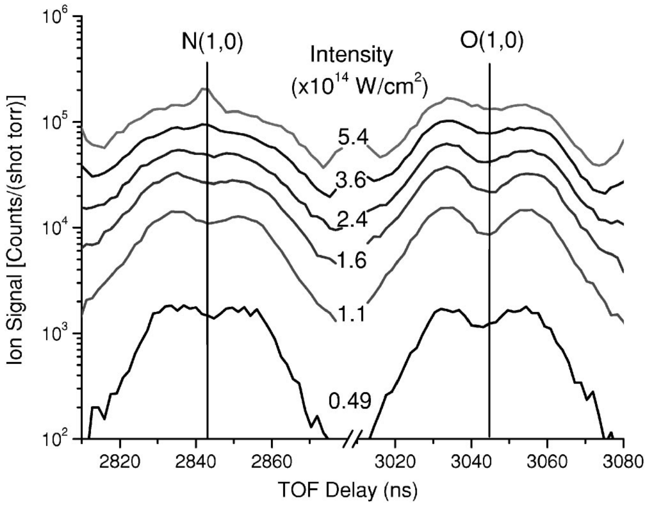

FIG. 2. TOF mass spectra of the N$^+$+O and N+O$^+$ channels in linearly polarized laser light at different intensities. The laser intensity increases by a constant ratio of 1.5 from the second lowest curve (1.1×10^{14} W/cm^2) to the highest one (5.4×10^{14} W/cm^2), except at the lowest intensity of 4.9×10^{13} W/cm^2.

The ionic channel, NO$^+$, in singly ionized NO has been studied previously [10], and so we confine our attention here to the behavior of the dissociation channels, N(1,0) and O(1,0). As shown in Fig. 2, TOF mass spectra are taken at different intensities across the delay range corresponding to the N(1,0) and O(1,0) channels. We can see that both N(1,0) and O(1,0) have a double-peak structure corresponding to the ions with initial velocity towards and away from the MCP detector at the end of the TOF drift tube. The initial kinetic energy release of the two dissociation channels can be determined from the flight time separation of the two peaks, as follows.

$$\mathrm{NO} \rightarrow \mathrm{N}^+ + \mathrm{O} + 0.35\ \mathrm{eV} \quad \mathrm{N}(1,0)\ \text{channel}$$

$$\mathrm{NO} \rightarrow \mathrm{N} + \mathrm{O}^+ + 0.46\ \mathrm{eV} \quad \mathrm{O}(1,0)\ \text{channel}$$

As illustrated in Fig. 3, our laser polarization is parallel to the TOF axis. The clear double-peak structure at lower intensities indicates that the molecules oriented along the laser polarization have the highest ionization and dissociation probability since electron ionization needs to overcome the least amount of potential energy along the molecular axis, due to a double-well molecular potential structure [3,11]. The central regions between the double peaks of both N(1,0) and O(1,0) channels correspond to ions with nearly zero initial kinetic energy along the TOF axis. Since NO molecules in the target region are randomly oriented, molecules oriented perpendicular to the laser polarization (see Fig. 3) may also be ionized and dissociate perpendicular to the TOF axis. These perpendicularly dissociated molecules will have a nearly zero kinetic energy on the TOF spectra, corresponding to the central regions of the N(1,0) and O(1,0) spectra. Note, our extraction region has an electric field strength of about 35 kV/m. Although the TOF extraction plate has a 1-mm-diameter pinhole to restrict volume average effects during ionization, this pinhole has little constraint for the two

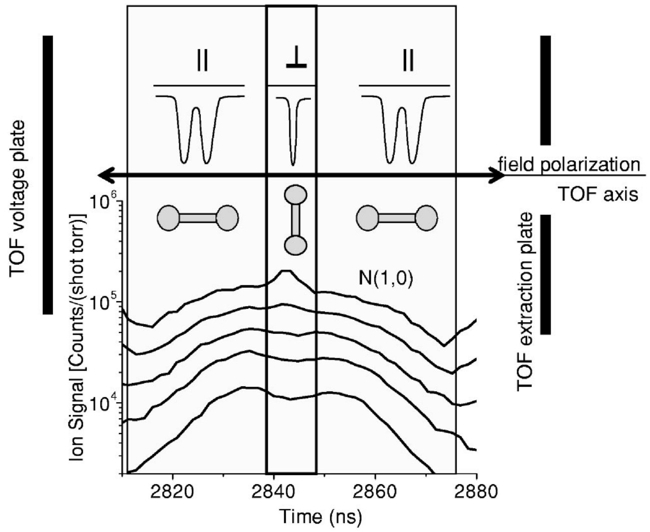

FIG. 3. Illustration shows that fragments with different kinetic energy correspond to molecular dissociation along different direction with respect to the laser polarization/TOF axis. N(1,0) peaks are used here for illustration. In the figure, the left and right regions correspond to the dissociation of molecules with their axis oriented along the laser polarization, while the central region corresponds to the dissociation of molecules with their axis oriented perpendicular to the laser polarization/TOF axis. Consequently, an electron will see a double-well and a single-well potential, respectively, when the molecules orient parallel or perpendicular with respect to the laser field (see text for details).

perpendicularly dissociated channels because of their small dissociation kinetic energy (0.35 and 0.46 eV, discussed above). This is confirmed by our kinetic and SIMION simulations [12].

It is well known that it is easier to ionize an electron along the molecular axis than perpendicular to the axis [3]. This can be qualitatively understood from Fig. 3, where an electron needs to overcome a shallower double-well potential barrier in the presence of a field along the molecular axis while a steeper atomic like single-well potential perpendicular to the molecular axis. Therefore, if the central regions in the N(1,0) and O(1,0) spectra are indeed from the NO molecules initially oriented perpendicularly to the laser polarization (TOF axis), these central peaks should become more visible only at higher intensities because electron ionization needs to overcome a greater potential energy in the perpendicular direction [3,11]. This is actually confirmed from our experimental observation in Fig. 2: as the intensity increases, the central part between the double peaks of N(1,0) and O(1,0) grows more and more pronounced. It is also possible that the central peaks in N(1,0) and O(1,0) are due to an accidental population of a lower-lying dissociation energy level that leads to a smaller dissociation energy. However, if this was the case, we would expect that the lower-lying energy level be populated more strongly at lower intensities rather than at higher intensities as we observed. Furthermore, the central peaks become progressively more and more pronounced as the laser intensity increases by an order of magnitude, and this indicates that the central peaks are more likely due to a general phenomenon (molecule random orientation as we discussed here) rather than accidentally populating to a lower-lying resonant energy level.

More interestingly, however, we note that the central part of N(1,0) grows faster than that of O(1,0), despite the fact that both channels are from the same precursor, singly ionized NO. Therefore, for molecules oriented perpendicular to the laser polarization, it appears that NO^+, if it dissociates, will preferably dissociate into N(1,0) rather than O(1,0). This is interesting, because the energy level of the former channel is actually higher than the latter channel by about 1 eV. A simplified estimate using the Ammosov-Delone-Krainov model [13] suggests that the 1 eV difference in ionization threshold could lead to 3–10 times the difference in ionization yield at our intensity range, and that is contrary to our experimental observation. To understand this, a more careful examination of strong-field-induced dissociation process for NO^+ is necessary.

Theoretically, it is very difficult to attain a general quantum mechanical description of an interacting system in the presence of a continuously varying nonperturbative strong field. During the strong interactions, it is not always possible to exactly characterize all the quantum processes involved, such as dipole coupling and field-dressed states. Some simple and intuitive pictures have found successes in interpreting strong-field phenomena. Noticeably, there are two such examples in the studies of strong-field interactions with atoms and molecules, respectively. For atoms, the rescattering model treats electrons as classical particles [14], and it has successfully accounted for many phenomena in field-atom interactions [1,2]. For molecules, detailed electronic structure effects have been shown to be a key factor in influencing a variety of strong-field phenomena [5–8,10]. Although not explicitly evident, both pictures can be considered as intuitive approximations of complicated quantum interactions in strong fields. Giving the complicated nature of strong field-molecule interactions, we approach the current problem in this paper by using the intuitive molecular picture that considers the detailed electronic structure effects in NO.

It is well known that the O atom has a greater electron affinity than the N atom and therefore, in NO molecules, the electrons in the 1π-binding orbital between the N and O cores should shift towards the O atom. Thus, a 1π electron closer to the N atom is less bound to the overall core potential than a 1π electron closer to the O atom (a simple calculation can illustrate this point). Therefore, a 1π electron closer to the N atom should be ionized more easily, and the removal of this N-side electron should result in the N(1,0) channel, as discussed earlier. This explains why the N(1,0) channel is easier to reach than the O(1,0) channel in strong fields. The next question, however, is why this observation is only seen in the central peaks that correspond to the electron ionization perpendicular to the molecular axis. We believe that the above-mentioned detailed electronic structure influence is most likely smeared out for ionization along the molecular axis since an electron needs to move through a double-well molecular potential that will complicate the ionization process [3,11]. The perpendicular ionization, on the other hand, should be more sensitive to the initial electronic structure since an electron only needs to overcome a simple atomiclike single-well potential. Thus, we see a higher central peak in N(1,0) than O(1,0) when molecules are oriented perpendicular to the field polarization/TOF axis. The consistency of our simply picture and the experimental observation differs drastically from what we may expect based on an energy level analysis, where the N(1,0) channel is supposed to be harder to reach than the O(1,0) channel.

To further understand why our observation is dramatically different from the energy-level predication, we provide the following hypothesis motivated by the concept discussed in Ref. [6]. As discussed in detail in Ref. [6], ionization dynamics is very different in strong fields compared to weak fields. Ionization in weak fields is a relatively slow process occurring over many cycles of laser light, while it occurs nearly instantaneously (within only a fraction of a half laser cycle) in the strong-field tunneling regime [6,13]. For strong-field ionization in NO, the initial electronic structure plays a crucial role. The fact that a 1π-bonding electron closer to the N atom is less bound to the overall core potential contributes to our experimental observation: ionization is easier for the N-side electron when molecules orient perpendicular to the laser polarization. The energy level of different channels, on the other hand, is based on experimental observations in weak fields under conditions where ionization typically is a relatively slow process, as discussed in detail in Ref. [6]. For weak-field ionization in NO, when an electron moves slowly away from the molecule, the remaining electrons have enough time to adjust their position to minimize their potential energy [6]. This electron readjustment during ionization will minimize the influence of initial electronic structure on ionization process. Therefore, as a more adiabatic process, electron ionization in weak fields should be easier from the O core since the ionization potential of the O atom is smaller than the N atom (13.62 eV for the O atom; 14.53 eV for the N atom) [15]. Thus, the O(1,0) channel is more energetically favorable in the weak field case, but the reversed case seems to be more applicable in strong-field ionization.

In summary, we have observed an apparently peculiar behavior in TOF mass spectra taken from the two dissociation channels of singly ionized NO molecules, N(1,0) and O(1,0). Both channels have a double-peak TOF structure with a smaller central peak that only becomes visible at relatively high intensities. We show that these central peaks are due to molecules dissociating with their axes perpendicular to the laser polarization/TOF axis. By studying these central peaks, we find that NO molecules, when oriented perpendicular to the laser polarization, preferentially dissociate to the N(1,0) channel rather than the O(1,0) channel, despite the fact that the latter channel is more energetically favorable in weak fields. A careful examination of the unique electronic structure of the NO molecule suggests that this observation is most likely due to the influence of the detailed electronic structure of NO on its strong field ionization dynamics, which leads NO^+ molecular ions created in strong laser fields to dissociate differently than they do in weak fields. While further studies are desirable to fully characterize this observation, our experiment suggests further evidence to reinforce our understanding of the fundamental differences between ionization dynamics in strong fields versus weak fields, as proposed in Ref. [6].

The author would like to acknowledge the support from the U.S. Air Force Office of Scientific Research.

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