## Charge Asymmetric Dissociation Induced by Sequential and Nonsequential Strong Field Ionization

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Charge asymmetric dissociation (CAD) is observed, for the first time, with near-infrared 30 fs laser pulses, in small molecules,  $N_2$  and  $O_2$ .  $N_2^{2+}$  is created by a nonsequential (vertical) transition and the dissociation fragments appear to be in excited states. Unlike  $N_2$ ,  $O_2^{2+}$  involves a sequential (nonvertical) transition. The charge asymmetric dipole coupling to the external field is insufficient to populate the charge transfer states leading to CAD. Rather, CAD is a natural result of strong field excitation and ionization. These results in the tunneling regime are also compared with previous experiments performed with UV radiation in the multiphoton regime. [S0031-9007(99)08736-0]

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The interaction of strong laser fields with atoms and molecules is of great interest when the laser field is strong enough to ionize many electrons during the short (femtosecond) interaction time. This interaction will lead to multielectron dissociative ionization (MEDI) in a molecule [1]. In the process of MEDI, after one or two electrons are ionized, the molecule starts to dissociate and the fragments repel each other. If additional electrons are stripped away, the ion fragments will continue to gain energy due to the Coulomb force. Therefore, the kinetic energy of these atomic ions determined from time-of-flight (TOF) spectroscopy reveals the dynamics of the MEDI process. It has been shown that the ionization rate reaches a maximum at the critical internuclear separation,  $R_c$ , where electron localization and enhanced ionization occur due to the double well potential of a molecule [2]. Charge symmetric dissociation (CSD), such as  $N_2^{2+} \rightarrow N^+ + N^+$ , appears to dominate the MEDI process if the molecule expands to the critical internuclear separation during the laser pulse.

Charge asymmetric dissociation (CAD), such as  $N_2^{2+} \rightarrow N^{2+} + N$ , is also seen but under more restricted conditions.  $N_2^{2+} \rightarrow N^{2+} + N$  has been observed following inner-shell ionization with soft x-ray radiation: the high energy photon leads to a vertical transition (i.e., no change in internuclear separation during the excitation or ionization) through an Auger process to a highly excited  $(N_2^{2+})^*$ state followed by CAD with a large kinetic energy release of 13.4 eV [3]. This CAD channel was also observed with high intensity UV (248 nm) laser radiation [4]. In addition, the observation of a new inner-orbital molecular transition at 55.8 nm in  $N_2^{2^+}$  induced by the same UV laser confirmed the reality of populating highly excited states by a strong nonlinear mode of coupling [5]. A more complete study of N<sub>2</sub> and O<sub>2</sub> was made with both 305 and 610 nm laser radiation [6,7]. The observation of fast  $N^{2+}$  ions from the CAD of  $N_2^{2+}$  in 305 nm light agrees with the two above-mentioned experiments [6]. Moreover, CAD was also found in O<sub>2</sub> but with a relatively low kinetic energy release ( $O_2^{2+} \rightarrow O^{2+} + O + 2.5 \text{ eV}$ ) [7]. However, both of these CAD channels were absent in the long wavelength (610 nm) radiation data.

It has been suggested that the states which lead to CAD are strongly coupled to the CSD states by a charge transfer transition [4,8,9]. The dipole, induced by the asymmetric displacement of the charge, interacting with the external field can provide this coupling [4,9]. The dissociation lifetime of the low lying states leading to CSD, therefore, is thought to be an essential parameter in determining the dynamics of the MEDI process [6]. At short wavelengths, the long lifetime states of  $N_2^{2+}$ , for example, are accessed, followed by vertical transitions to states leading to CAD. At longer wavelengths, however, states with dissociation lifetimes shorter than the pulse duration are thought to be populated, leading to nonvertical ionization and symmetric fragmentation. This is the hypothesis proposed to explain the different behavior of CAD in short and long wavelength radiation as reported in Ref. [6].

The observations of CAD of I<sub>2</sub> in long wavelength (800 nm) radiation with pulse durations under 100 fs have revealed the possibility of CAD with low energy photons [9,10]. Furthermore, it is supposed that CAD in molecules smaller than I<sub>2</sub> will occur with a pulse duration shorter than the time required for the molecule to reach  $R_c$ . In this paper, we report, for the first time with near-IR radiation, the observation of the CAD of  $N_2^{2+}$  and  $O_2^{2+}$  using 30 fs 800 nm Ti:sapphire laser pulses. More significantly, unlike the previous observations in the soft x ray and the UV [3,4,6,7], the N<sup>2+</sup> fragment has a low kinetic energy. However, like the previous observations, the formation of the CAD states of  $N_2^{2+}$  involves a vertical transition. In contrast, the CAD of  $O_2^{2+}$  involves a nonvertical excitation process, and it has a kinetic energy release similar to that reported in Ref. [7]. Furthermore, the threshold intensity of these two channels is not enough to provide the dipole coupling to populate the CAD states. These results rule out the hypothesis of a dipole coupling to the charge transfer states and provide evidence that CAD is the natural result of strong field excitation and ionization.

The laser used in the experiment is a Ti:sapphire system running at a 1 kHz repetition rate, producing over 400  $\mu$ J/ pulse in 30 fs pulses with a center frequency of 800 nm [10,11]. The ion fragments are analyzed with a standard TOF mass spectrometer [12]. An angular collection efficiency factor is obtained experimentally to take into account the three-dimensional angular distribution of each fragment channel.

Figure 1 shows the TOF spectrum of  $N^{2+}$  at an intensity of  $7.5 \times 10^{14}$  W/cm<sup>2</sup>. In general, the  $X_2^{(q1+q2)+} \rightarrow X^{q1+} + X^{q2+}$  dissociation channel is labeled as  $X(q_1, q_2)$ . Using correlations, the outer two pairs of peaks in Fig. 1 are identified as the N(2,1) and N(2,2) channels. There is no correlation between the two inner small peaks, and neither of these peaks is correlated to an N<sup>+</sup> signal. Therefore, the inner peaks are considered to come from the CAD channel N(2,0). The kinetic energy release of N(2,0) is determined from the flight time separation of the two peaks. The resulting process is

$$N_2^{2+} \rightarrow N^{2+} + N + 1.5 \text{ eV}.$$
 (1)

It should be noted that the small kinetic energy release 1.5 eV is quite different from the high energy release (more than 10 eV) in the previous observation using the UV radiation [4].

It is natural to think that the low dissociation energy of the N(2,0) channel might result from a nonvertical transition [13]. However, this question can be answered experimentally by determining whether Eq. (1) proceeds through sequential or nonsequential ionization: if the double ionization is sequential, the internuclear separation can change during the ionization process allowing for a nonvertical transition, while simultaneous or nonsequential double ionization (NSDI) would require a vertical transition. Sequential double ionization is easily distinguished from NSDI



FIG. 1. Time-of-flight spectrum of  $N^{2+}$  with linearly polarized light at an intensity of  $7.5 \times 10^{14} \text{ W/cm}^2$ . The  $N_2^{(q1+q2)+} \rightarrow N^{q1+} + N^{q2+}$  dissociation channel is labeled as  $N(q_1, q_2)$  and similarly for the other figures. The low energy peaks are shown enhanced by a factor of 10.

by utilizing a well-established technique from the study of atoms in strong laser fields [14,15] based on the intensity dependence of the ratio of  $X^{2+}/X^+$ , where  $X^+$  and  $X^{2+}$  are the ion yields for single and double ionization of the atom or molecule X (e.g.,  $N_2^{2+}/N_2^+$  can show NSDI in a molecular system [15]). If  $X^{2+}$  is produced in a sequential process,  $X^+$  will be the intermediate species and the ratio  $X^{2+}/X^+$  will reflect just the ionization rate from  $X^+$  to  $X^{2+}$  which will have a strong intensity dependence. However, if this ratio only weakly depends on intensity, it shows that the precursor to  $X^{2+}$  is not  $X^+$  and the ionization must be nonsequential. Figure 2 shows the relevant ion yields, while in Fig. 3 the weak dependence of the ratio of N(2,0)/N<sub>2</sub><sup>+</sup> on intensity below  $3.5 \times 10^{14}$  W/cm<sup>2</sup> shows that N(2,0) is formed through NSDI. This ratio approaches the sequential ion yield of N(2,0) when the intensity is higher than  $3.5 \times 10^{14} \text{ W/cm}^2$ , because, at that point, the ionization to  $N_2^+$  has saturated. The ratios of  $N(2,0)/N_2^{2+}$  (metastable) and N(2,0)/N(1,1) are also plotted in Fig. 3. By the same reasoning, the fact that these ratios are nearly independent of intensity further shows that there is no coupling between the CAD and the metastable or CSD states. This rules out the hypothesis that the CAD states have to be populated through the metastable or CSD states. Thus, the vertical transition in forming the N(2,0)can be expressed as

$$N_2 \rightarrow (N_2^{2+})^* + 2e^- \rightarrow N^{2+} + N + 2e^-.$$
 (2)



FIG. 2. Ion yields with error bars for  $N_2^+$ ,  $N^{2+}$  from N(2,0),  $O_2^+$ , and  $O^{2+}$  from O(2,0) with linearly polarized light.



FIG. 3. Intensity dependent ratio curves with error bars for  $N(2,0)/N_2^+$ ,  $N(2,0)/N_2^{2+}$  (metastable), N(2,0)/N(1,1), and  $O(2,0)/O_2^+$ .

However, there is no low lying N(2,0) state documented which results in only a 1.5 eV kinetic energy release for this vertical transition [3]. Therefore, if the same CAD states are populated as in the UV experiments, the difference in kinetic energy release must go into electronic excitation of the fragments.

Figure 4 shows the TOF spectrum of  $O^{2+}$  at an intensity of  $4 \times 10^{14}$  W/cm<sup>2</sup>. Again, the inner peaks are considered coming from the CAD channel O(2,0) based on their lack of correlation with any other peaks. The kinetic energy release of 2.0 eV for O(2,0) agrees relatively well with the observation in Ref. [7] (2.5 eV, discussed above). The result is

$$O_2^{2^+} \to O^{2^+} + O + 2.0 \text{ eV}.$$
 (3)

The ion yield of O(2,0) and the intensity dependence of the ratio  $O(2,0)/O_2^+$  are also plotted in Figs. 2 and 3, respectively. The ratio curve for O(2,0) drops monotonically and does not show any signature of NSDI, indicating that the O(2,0) channel is accessed by a nonvertical transition, as opposed to N(2,0) discussed above. Furthermore, we must consider the possibility that the nonvertical channel O(2,0) results from postdissociation ionization (PDI) of O(1,0). However, the O(1,0) channel is produced as follows:

$$O_2 \to O_2^+ + e^- \to O^+ + O + e^- + 3.6 \text{ eV}.$$
 (4)

The kinetic energy release of 3.6 eV for O(1,0) is actually higher than the 2.0 eV for O(2,0), and this indicates that PDI does not play any significant role in forming the CAD



FIG. 4. Time-of-flight spectrum of  $O^{2+}$  with the linearly polarized light at an intensity of  $4 \times 10^{14}$  W/cm<sup>2</sup>.

channel O(2,0). It is interesting to note that this relation is quite unique for O<sub>2</sub> because the kinetic energy of the (1,0) channel is normally smaller than the (2,0) channel in other molecules, such as N<sub>2</sub>, reported here, and I<sub>2</sub>, in Ref. [10]. Therefore, the O(2,0) is formed through a stepwise process which can be shown as

$$O_2 \to O_2^+ + e^- \to (O_2^{2+})^* + 2e^- \to O^{2+} + O + 2e^-.$$
(5)

The ionization threshold leading to the CAD channels is determined by summing the following contributions: the energy necessary to dissociate the neutral molecule, the energy needed to ionize each atom to its specific charge state, and the released kinetic energy. The resulting total energy is the energy level of the fragment channels if we assume the dissociating fragments are in their ground state and, thus, only gives a lower bound. The ionization thresholds obtained by this method for N(2,0) and O(2,0)are 55.3 eV and 56.1 eV, respectively, above the neutral molecule ground state. These thresholds are at least 10 eV above the corresponding CSD(1,1) channel and metastable states. The ion yield curves of N(2,0) and O(2,0) in Fig. 2 show that the threshold intensities of these two CAD channels are both around  $1.2 \times 10^{14} \text{ W/cm}^2$ . The dipole coupling energy at this intensity is  $\Delta E_{\rm th} = RF \simeq 3.6 \text{ eV}$ , where F is the threshold field strength and R is the equilibrium internuclear separation, 1.2 Å, for N(2,0), since it is a vertical transition. The exact internuclear separation of O(2,0) is not known because it involves a nonvertical transition. However, its dipole interaction energy is also estimated to be less than 10 eV, which is the minimum energy needed to couple the CSD and CAD states. Therefore, we demonstrate that the charge asymmetric dipole coupling cannot provide sufficient energy to populate the charge transfer states from the CSD states in these small molecules.

Since we rule out the explanation of the dipole interaction with the external field to populate the charge

transfer states, the formation of CAD must be a natural consequence of nonresonance strong field excitation. In fact, the diverse pathways leading to the CAD states, the vertical transition in N(2,0), the nonvertical transition in O(2,0), and the various channels in  $I_2$  in Ref. [10], show the generality of intense field induced CAD. When the pulse duration is long enough allowing the molecule to expand to the critical internuclear separation  $R_c$ , tunneling ionization seems to favor the CSD channels. Therefore, this first observation of CAD in small molecules, N2 and O<sub>2</sub>, must be due to the short pulse duration (30 fs) of our laser system. However,  $R_c$  is only an important parameter in molecular tunneling ionization and does not play a significant role in multiphoton ionization (MPI). This explains why CAD can still be observed with long pulse  $(\sim 0.5 \text{ ps})$  lasers in the UV, since the Keldysh parameter is proportional to the radiation frequency for a particular intensity [16]. Therefore, the UV interaction is dominated by MPI and does not depend on  $R_c$ .

Finally, the interesting observation of a relatively low kinetic energy release for N(2,0) in our ultrashort IR radiation compared to the large kinetic energy release seen in the soft x ray and UV radiation experiments indicates that the N(2,0) fragmentation channel itself is an excited state. If this is indeed true, the dissociation dynamics must be quite different for the long and short wavelengths, as illustrated schematically in Fig. 5. The ground state of N(2,0) can be populated through a vertical transition to point a in both IR and UV radiation. If there is a shallow excited state curve lying above the ground state by an IR photon energy near point a, the population transfer from a to b will be very efficient resulting in a low kinetic energy release. With UV radiation, the ground and excited states will be coupled at point c. However, the probability for making a transition at this point will be reduced because of two effects: point c will be reached later in the laser pulse when the intensity is lower, and the N(2,0) fragments acquire a certain amount of kinetic energy through dissociation. Both of these effects weaken the transition to the excited state in accordance with Landau-Zener theory, in which the transition probability depends on the strength of the coupling and the speed of the crossing. This can explain the observation of the fast N(2,0) peaks using UV radiation and the slow peaks in IR radiation. However, the validity of this explanation requires further investigation.

In summary, with 30 fs 800 nm ultrashort pulse radiation, for the first time with near-IR radiation, we observe CAD in small molecules,  $N_2$  and  $O_2$ . The insufficient dipole energy to populate the CAD channels through the charge transfer coupling and the diverse pathways producing CAD lead us to conclude that CAD is a general result of strong field excitation and ionization not limited



FIG. 5. Schematic potential energy curves for the ground and excited states of N(2,0).

to the dipole coupling. The slow fragmentation of the N(2,0) channel may indicate that the CAD of N(2,0) leaves the fragments in an excited state and this requires further investigation. Moreover, the quite different behavior of N(2,0) and O(2,0) has to be related to the different electronic structures of N<sub>2</sub> and O<sub>2</sub> as reported in Ref. [15]: N<sub>2</sub> has a closed shell electronic structure, while the outermost orbital  $(1\pi_g)^2$  of the ground state O<sub>2</sub> is only half filled. The detailed electronic structure leads to different behaviors of molecules interacting with strong laser fields.

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