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The dissociation pathways of N_2^+ in intense femtosecond laser fields*

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Using a neutral N_2 beam as target, this paper studies the dissociation of N_2^+ in intense femtosecond laser fields (45 fs, $\sim 1\times10^{16}$ W/cm^2) at the laser wavelength of 800 nm based on the time-of-flight mass spectra of N^+ fragment ions. The angular distributions of N^+ and the laser power dependence of N^+ yielded from different dissociation pathways show that the dissociation mechanisms mainly proceed through the couplings between the metastable states (A, B and C) and the upper excited states of N_2^+. A coupling model of light-dressed potential energy curves of N_2^+ is used to interpret the kinetic energy release of N^+.

Keywords: dissociation mechanisms, intense femtosecond laser fields, time-of-flight mass spectra
PACC: 7970, 3280K, 3520X

1. Introduction

When a single electron is removed from a diatomic molecule by an intense laser pulse, the parent molecular ion can dissociate into a neutral atom and an ion. For the simplest molecular ion of H_2^+, the mechanisms of dissociation such as bond softening, bond hardening and above threshold dissociation are well understood.[1−3] These phenomena have been explained in terms of the light-dressed potential energy curves (PECs) consisting of the two lowest lying electronic states, $1s\sigma_g^+$ and $2p\sigma_u^+$, both of them are strongly coupled by n photons corresponding with emission or absorption of extra photons in intense laser fields.[4,5] However, for the multielectron diatomic molecules, multiple couplings should be included among a number of electronic states because of the complex electronic structure in comparison with H_2^+.

Some studies have been well done on the laser-induced dissociation of Na_2^+[6,7] and O_2^+.[8,9] To determine the dissociation pathways of the molecular ions, four conditions in brief[9] should be considered. First, the intensity $I_{\rm pred}$ at which a dissociation feature is predominant, is related to the sum of absorbed and emitted photons, n, required along the pathway, i.e., higher n corresponds to higher $I_{\rm pred}$. Second, the shape and position of the kinetic energy release (KER) peak generated by a particular pathway is influenced by the shape of the PECs comprising it. Third, the number of transitions favouring internuclear alignment parallel and perpendicular to the laser polarization required along a pathway will determine the angular distribution of the channel. Fourth, all transitions involved in a pathway must obey the molecular dipole selection rules.

Very recently, Gaire and co-workers[10] report their research on the dissociation of N_2^+ beam by intense laser pulses (7 fs) at 790 nm. In addition to the usual low-KER peak (∼0.6 eV), a high-KER peak (∼6.1 eV) is first observed. The phenomena are explained by the coupling between the electronic ground sate and highly excited states of N_2^+ because the N_2^+ beam target is predominantly in its electronic ground state and vibrationally cold.

This paper investigates the dissociation pathways of $N_2^+ \rightarrow N^+ + N$ in intense laser fields (45 fs, $\sim 1\times10^{16}$ W/cm^2). It should be mentioned here that we use a neutral N_2 beam target in our experiment. The N_2 molecule is ionized to produce the N_2^+ ion and then the N_2^+ ion interacts with the same laser pulse. In addition to the ground state, the N_2^+ molecular ion can be in excited states when the intense laser field removes an inner-valence electron of

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N_2. The $A^2\Pi_u$ state and the $B^2\Sigma_u^+$ state of N_2^+ have been first observed in the photo-electron spectrum of N_2.[11] The further information of the $B^2\Sigma_u^+$ state has also been provided by reports[12,13] on the observation of photo-emission spectra of the first negative band system of N_2^+. The $C^2\Sigma_u^+$ state has been identified by vacuum ultraviolet fluorescence spectroscope.[14] We determine the dissociation pathways resulting from the couplings between the metastable states (A, B and C) and the upper excited states of N_2^+ and interpret the KER (< 2.5 eV) of N^+ using the light-dressed PECs in the diabatic Floquet representation.

2. Experimental details

Figure 1 shows the experimental setup for studying the interaction between the molecular beam and intense laser fields. The laser pulses are provided by a commercial Coherent Inc. legend-UPS Ti: sapphire chirped-pulse amplification laser system with a central wavelength of 800 nm, a 1 kHz repetition rate and one pulse energy of about 1.8 mJ. The output of the pulse duration with a Fourier-transform-limited near 35 fs full width at half height (FWHM) is broadend to 45 fs at the target. The linearly polarized laser beam is focused by an $f = 65$ mm aspheric lens into the interaction point in the vacuum chamber. The focus of the laser beam has a Gaussian shape in space with a $1/e^2$ diameter of 23 μm measured by a CCD camera. The Raleigh length is about 0.53 mm. The maximum peak intensity of the laser at the focusing point is estimated to be near 1×10^{16} W/cm^2. The peak intensity and the laser polarization direction can be continuously changed using a combination of a half-wave plate and a polarizer.

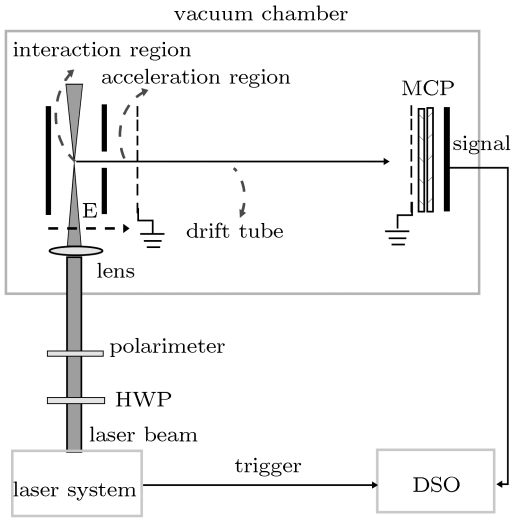


Fig.1. Schematic diagram of the experimental setup.

A standard Wiley–Mclaren time-of-flight (TOF) mass spectrometer[15] is mounted in the vacuum chamber with a residual background gas pressure of 5×10^{-5} Pa. Nitrogen gas is introduced into the interaction region via a supersonic nozzle to a chamber pressure of 2×10^{-4} Pa to avoid space-charge effect. Ions produced in the interaction region are extracted through a small slit (0.3 mm width) on the extraction electrode plate by a weak electric field (400 V/cm). The small slit can ensure only a small slice of the total focal volume which is sampled to improve spatial resolution and also meet the conditions of the intensity difference spectra (IDS) method.[16] The IDS method allows one to eliminate the contributions from lower intensity and determines the exact contributions from a given intensity region. The extracted ions pass through an acceleration region and a 120.5 cm drift tube to the microchannel plate detector. The output signals from the detector are recorded by a 1 GHz digital storage oscilloscope and the signal averaged over a number of 500 laser shots.

3. Results and discussions

3.1. Experimental data and theoretical potential energy curves

Figure 2 shows the observed TOF mass spectra of N^+ for three intensity slices using the IDS method with the laser polarization parallel to the TOF axis. The peak maximum intensity I_0 is near 1×10^{16} W/cm^2 at the focusing point. The peak labeled as α with near zero kinetic energy is attributed to N_2^{2+} having the same mass-to-charge ratio as N^+. With the different kinetic energy distributions, the peaks β and γ correspond to N^+ originating from different dissociation channels of N_2^+. The dissociation pathway β is predominant in Figs.2(b) and 2(c), but the dissociation pathway γ is predominant and extends to higher energies in Fig.2(a). These features suggest that the dissociation pathways of N_2^+ depend on the focusing intensities of the laser pulses.

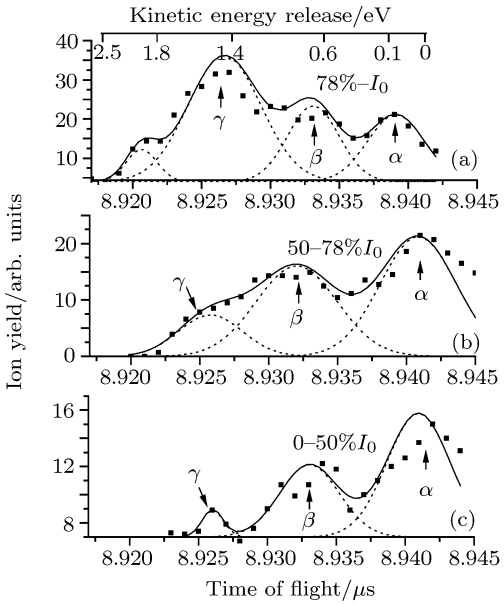


Fig.2. The TOF mass spectra of N^+ from N_2^+ dissociation for three intensity slices with the laser polarization along the drift tube. The dots represent the experimental data, the dot lines are obtained using the multi-Gaussian fitting method and the solid lines are the envelopes. I_0 is the peak intensity near 1×10^{16} W/cm^2. The energy scale shows the released kinetic energy. The dissociation pathways corresponding to the KER peaks labeled as α, β and γ are discussed in this paper.

The electronic ground state configuration of the N_2 molecule is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$. The N_2^+ ions produced due to the interaction with an intense laser field are expected in the ground state associated with the removal of an outer-valence electron and the excited states associated with the removal of an inner-valence electron of N_2. For the excited states of N_2^+, we only consider the metastable states ($A^2\Pi_u$, $B^2\Sigma_u^+$, $C^2\Sigma_u^+$) according to experimental evidence.[11–14] The initial vibrational population of N_2^+ from the multiphoton ionization of N_2 has been calculated by Becker *et al.*[17] They found that the lowest vibrational levels are more strongly populated (while the higher levels are less populated) by the laser interaction than in Franck–Condon distributions. For example, the ground vibrational level ($v = 0$) is highly populated (larger than 95% of the total vibrational population) for the $X^2\Sigma_g^+$ state as well as for the $B^2\Sigma_u^+$ state. For the $A^2\Pi_u$ state, the vibrational levels (from $v = 1$ to 3) occupy over 95% and less population in the $v = 4$ vibrational level. These features can further help us to reduce the possible dissociation pathways. Figure 3 shows the PECs of the doublet states of N_2^+ calculated by Hiyama and Iwata,[18] also by Aoto and Ito *et al.*[19] These authors have calculated other doublet states which are not represented in the figure for more clarity in the present discussion.

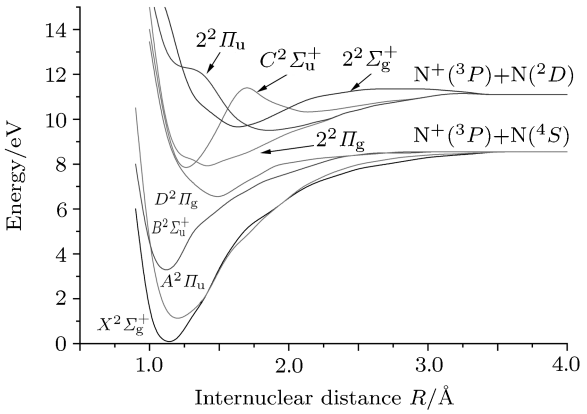


Fig.3. Potential energy curves of the doublet states of N_2^+.

3.2. Determining laser-induced dissociation pathways

In the diabatic Floquet representation, the diabatic light-dressed PECs, which are formed through the coupling between initial molecular states {i} and photon-field states {N}, are denoted by {i$\pm n\omega$} where '+' or '–' corresponds to the shifting of molecular PECs up or down by the energy of the n photons (i.e., $\pm n\hbar\omega$), respectively. The diabatic light-dressed PECs can provide a clear insight to explore possible dissociation pathways of molecular ions in intense laser fields.[6]

The angular distribution of photodissociation fragments of a diatomic molecule can be expressed by a product of these functions $\cos^{2n}\theta \sin^{2m}\theta$, where θ is defined as an angle between the laser polarization and the internuclear axis of the molecule, n and m are the number of photons emitted and absorbed in parallel and perpendicular transitions along the pathway, respectively.[8] It is noted that the measured angular distributions can be modified by laser-induced molecules (or molecular ions) alignment effects if the femtosecond laser pulse is not sufficiently shot in experiment. However, it has been indicated that this phenomenon is less important for N_2 molecules or N_2^+ ions.[20] In the following presentations, the alignment effects are negligible for N_2^+ ions, i.e., the N_2^+ ions is in random alignment both during and after the laser pulse.

Figure 4(a) shows the angular distribution of the peak β. The lines labeled as L_1, L_2 and L_3 are fitted to the experimental data. The line L_1, i.e., a $\cos^{14}\theta$ function with $n = 7$ (dash-dot line) in Fig.4(a), corresponds to the angular distribution of a parallel transition from the initial ground state $X^2\Sigma_g^+$ to the final state $C^2\Sigma_u^+ - 7\omega$. The dissociation pathway that produces a KER of $\sim$ 0.6 eV has been identified in Ref.[10]. The line L_1 is lower than the experimental data (black dots in the left panel) in Fig.4(a) and it suggests that other dissociation channels contribute to the angular distribution. A candidate dissociation pathway is the parallel transition from the $A^2\Pi_u$ state near $v = 0$ to the dressed $D^2\Pi_g - 5\omega$ state through 5-photon gap shown in Fig.4(b), producing a KER of about 0.6 eV. The $v = 1$ vibrational level of the $A^2\Pi_u$ state also contributes to the peak and it shifts the KER distribution to higher value in Fig.2. The $A^2\Pi_u \rightarrow D^2\Pi_g - 5\omega$ dissociation pathway yields a $\cos^{10}\theta$ ($n = 5$) angular distribution labeled as line L_2 (dotted line) which is a better fit to the data (left panel) in Fig.4(a). It is worth noting that, although the $A^2\Pi_u \rightarrow 2^2\Pi_u - 6\omega$ parallel transition can also yield a KER of about 0.6 eV shown in Fig.4(b), the channel makes a very small contribution to the angular distribution in Fig.4(a) because more photons for the coupling and high vibrational level ($v = 4$) of the $A^2\Pi_u$ state are needed. The angular distribution, corresponding to the experimental data (black dots in the right panel) in Fig.4(a), is well fitted by a $\sin^{10}\theta$ ($n = 5$) function labeled as line L_3 (solid line). It is a perpendicular transition from the $B^2\Sigma_u^+$ state near $v = 1$ to the dressed $2^2\Pi_g - 5\omega$ state shown in Fig.4(c), yielding a KER of about 0.3 eV which is not shown in Fig.2 because of the perpendicular transition feature. The dissociation pathway $B^2\Sigma_u^+ \rightarrow 2^2\Pi_g - 5\omega$ is different from the dissociation pathway $X^2\Sigma_g^+ \rightarrow D^2\Pi_g - 6\omega$ which yields a KER of about 1.0 eV in Ref.[10]. We also eliminate the dissociation channel $A^2\Pi_u \rightarrow C^2\Sigma_u^+ - 6\omega$, which produces a KER of about 0.4 eV, because more photons for the coupling and the high vibrational level ($v = 5$) of the $A^2\Pi_u$ state are required to overcome this barrier of the $C^2\Sigma_u^+$ state at an internuclear distance about 1.69 Å. Compared to the dissociation pathway $A^2\Pi_u \rightarrow D^2\Pi_g - 5\omega$ with the dissociation limit $N^+(^3P)$+$N(^4S)$, the dissociation pathway $B^2\Sigma_u^+ \rightarrow 2^2\Pi_g - 5\omega$ dissociates to the $N^+(^3P)$+$N(^2D)$ limit. The dissociation channels with peaks at a KER of $\sim$0.6 and $\sim$0.3 eV, namely, pathway β, are predominant in the lower intensities.

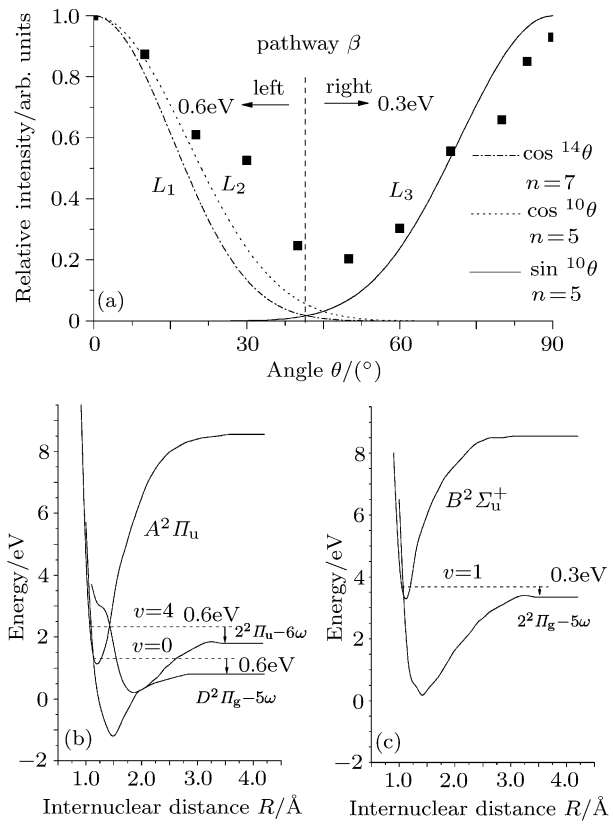


Fig.4. The measured angular distribution for the peak β where θ is the angle between the molecular axis and the laser polarization direction. The lines labeled as L_1, L_2 and L_3 are fits to the experimental data in (a). Light-dressed PECs of N_2^+ illustrating the dissociation pathway β that leads to a KER of $\sim$0.6 eV in (b) and $\sim$0.3 eV in (c) (see text). The wavelength 800 nm corresponds to single-photon energy 1.55 eV.

Figure 5(a) shows the measured angular distribution (black dots) of the peak γ which produces a KER of $\sim$ 1.4 eV in Fig.2. The dash-dot line, i.e., a $\cos^{16}\theta$ ($n = 8$) function in Fig.5(a), corresponds to the angular distribution of the parallel transition from the $X^2\Sigma_g^+$ state to the dressed $2^2\Sigma_g^+ - 8\omega$ state. The dissociation pathway $X^2\Sigma_g^+ \rightarrow 2^2\Sigma_g^+ - 8\omega$, yielding a KER of $\sim$ 1.6 eV, has also been determined by Gaire *et al.*[10] The channel γ observed in our experiment is not the same as the pathway $X^2\Sigma_g^+ \rightarrow 2^2\Sigma_g^+ - 8\omega$ in Ref.[10] though both of the channels have a similar KER. Two reasons are considered here. First, the $\cos^{16}\theta$ angular distribution has a great departure from the angular distribution of the dissociation channel γ (black dots) in Fig.5(a). Second, an obvious characteristic is that the N^+ yield from the dissociation pathway with a KER of $\sim$0.6 eV is predominant in the 6.5×10^{14} W/cm^2 and 6.0×10^{15} W/cm^2 laser

intensities in Ref.[10]. However, in our experiment, the N^+ yield from the dissociation pathway γ with a KER of ∼1.4 eV increases rapidly along with the laser intensities and exceeds that from the dissociation pathway β with a KER of ∼0.6 eV when the laser intensity is near I_0 in Fig.2. The above two reasons imply that the channel γ is different from the dissociation pathway $X^2\Sigma_g^+ \rightarrow 2^2\Sigma_g^+ - 8\omega$. The angular distribution of the pathway γ is well fitted by a $\cos^6\theta$ ($n = 3$) function (solid line) in Fig.5(a). The most likely candidate is the dissociation pathway from the $C^2\Sigma_u^+$ state to the dressed $2^2\Sigma_g^+ - 3\omega$ state transition because the $A^2\Pi_u$ state and the $B^2\Sigma_u^+$ state coupling to the upper excited states of N_2^+ need more than five photons. Figure 5(b) shows the dissociation pathway $C^2\Sigma_u^+ \rightarrow 2^2\Sigma_g^+ - 3\omega$ that yields a KER of ∼1.5 eV consistently with the experimental measurement in Fig.2. The $v = 1$ vibrational level also contributes to the peak γ and extends the KER to ∼1.8 eV.

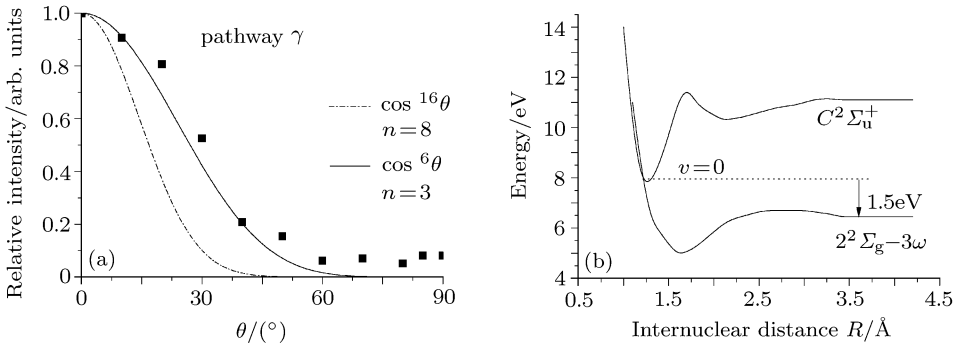


Fig.5. (a) The measured angular distribution for the peak γ where θ is the angle between the molecular axis and the laser polarization direction. The dash-dot line and solid line are fitted to the experimental data (black dots). (b) Light-dressed PECs of N_2^+ illustrating the dissociation pathway γ which leads to a KER of ∼1.5 eV (see text). The wavelength 800 nm corresponds to single-photon energy 1.55 eV.

4. Conclusion

The dissociation of N_2^+ in tense laser fields (45 fs, $\sim 1 \times 10^{16}$ W/cm^2) is investigated based on the TOF mass spectra of N^+ fragment ions by using neutral N_2 beam target. It is clear that the dissociation channels corresponding to different KER distributions depend on the focusing intensities of the laser pulses by the IDS method. We find the dissociation mechanisms mainly through the couplings between the metastable states (A, B and C) and the upper excited states of N_2^+, which is different from the conventional concept that the dissociation mainly results from the ground state coupling to the upper excited states. We identify the dissociation pathways by the angular distributions of N^+ and interpret the KER using the diabatic light-dressed PECs of N_2^+. Our experimental results are different from those of Ref.[10], which also show the fact that the neutral beam target and ion beam target can make them complementary approaches to understanding the dynamics of molecules in intense laser fields.[21]

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