Few-Photon Multiple Ionization of N_2 by Extreme Ultraviolet Free-Electron Laser Radiation

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(Received 19 November 2008; published 25 March 2009)

Few-photon multiple ionization of N_2 was studied differentially in a reaction microscope using 44 eV, ~25 fs, intense (~10^{13} W/cm^2) photon pulses from FLASH. Sequential ionization is observed to dominate. For various intermediate charge states N_2^{n+} we find a considerable excess of photons absorbed compared to the minimum number that would energetically be required. Photoionization of aligned N_2^{n+} ions, produced by photon absorption in sequential steps, is explored and few-photon absorption pathways are traced by inspecting kinetic energy releases and fragment-ion angular distributions.

DOI: 10.1103/PhysRevLett.102.123002 PACS numbers: 33.80.−b

Absorption of extreme ultraviolet (EUV) radiation by simple molecules like N_2 or molecular ions is of paramount importance for the physics and chemistry of planetary upper atmospheres [1], of interstellar clouds [2], possibly for the existence of life and has widespread applications in technical plasmas. Accordingly, it has been investigated in numerous studies at 3rd generation synchrotron radiation facilities.

Ultrabrilliant, short-pulse radiation sources of the next generation, such as the free-electron laser (FEL) in Hamburg (FLASH) [3] or the EUV Spring8 Compact SASE Source (SCSS) [4], now open a new chapter exploring this interaction in regimes that have so far been inaccessible. Thus, few EUV-photon induced multiple ionization (MI) of molecules can be investigated for the first time, photoionization of aligned and polarized molecular ions might be explored and the interaction of EUV photons with highly excited molecules or molecular ions may become accessible. Along these lines, the dissociation of a molecular ion, HeH^+, after absorption of a 38.7 eV photon has been investigated [5] recently, MI total cross sections were studied at FLASH [6,7], and two-photon absorption was established at SCSS [8] (see also [9] for high harmonic sources).

In this Letter we report on MI of N_2 induced by few EUV-photons at 44 eV via complete fragment-ion-momentum imaging. We observe sequential absorption of up to five photons within ~25 fs, measure the kinetic energy releases (KER) and fragment-ion angular distributions (FIAD) of numerous dissociating or Coulomb-exploding states and obtain information on absorption alignment. N_2 was chosen since it has been investigated in utmost detail in the past. Previous studies include interactions with single EUV photons [10–14], collisions with electrons and ions [15], ionization in ultrashort intense visible laser fields [16] as well as pump-probe experiments with EUV pulses [17].

Our experiment, a dedicated reaction microscope [18], was installed at the focus (~30 μm diameter) of beam line BL 2 at FLASH. With single pulse energies of a few μJ, peak intensities of $I \cong 10^{13}$ W/cm^2 were reached at 44 ± 0.5 eV, a pulse-train repetition rate of 5 Hz and 12 or 24 microbunches (time interval 10 μs) per train. The energy of each individual FLASH pulse was recorded and the corresponding intensity was estimated with an uncertainty of about a factor of 5 from the focus diameter and the pulse length (see Ref. [19]). The linearity of this procedure was confirmed by inspecting the linear increase of the H_2^+ yield generated by one-photon absorption (see Fig. 2). The light beam intersected a well-collimated (1 mm diameter) and intrinsically cold supersonic molecular N_2 gas jet propagating transverse to the photon beam direction with densities of up to 10^{10} molecules/cm^3. Ionic fragments were projected by means of an electric field (35 V/cm) onto a time- and position-sensitive MCP-detector (diameter 120 mm, position resolution 0.1 mm, delay-line readout). From the measured TOF and position of each individual fragment the initial momentum vectors were reconstructed. The detector dead time between two subsequent events was about 20 ns.

Because of the quite short dissociation times of most of the highly excited N_2^* as well as N_2^{n+} molecule states (see Fig. 1), typically below 100 fs (with the exception of some metastable levels) as compared to the typical rotation period of ~10 ps, the direction of motion for the ionic fragments directly reflects the spatial alignment of the parent molecules (molecular ions) at the instant of photoionization. Therefore, measuring FIADs and KERs for the fragmenting ions simultaneously allows one to investigate in detail the dynamics of photoabsorption.

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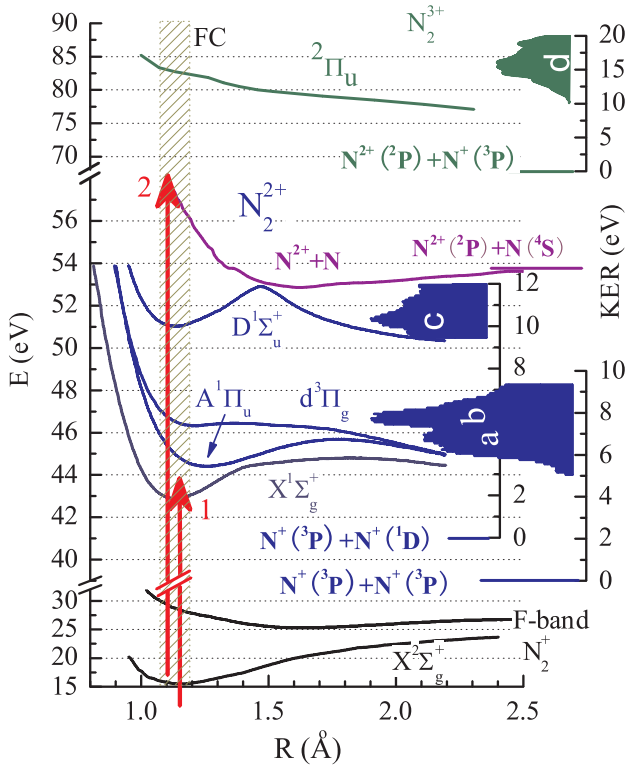

FIG. 1 (color online). Illustration of the dominant dissociative multiple ionization pathways of N_2 and the KER spectra of coincident ionic fragments N^+/N^+ and N^+/N^{2+} for double (blue and violet) and triple (green) ionization, respectively. Potential curves are taken from [10,15,22,27]. Three N_2^{2+} dissociation states are clearly visible in the KER spectra plotted in the right of this figure, marked as (a), (b), and (c), respectively. The KER spectrum labeled *d* corresponds to dissociation of the $^2\Pi_u$ state of N_2^{3+} [22]. The Frank-Condon regime (vertical shaded band) and two-photon transitions (vertical arrows) are sketched.

Double ionization (DI) by EUV photons has been explored in some detail in differential experiments for He and Ne atoms and distinct signatures for two different multiphoton absorption pathways; i.e., sequential (SI) and direct nonsequential ionization (NSI) have been observed in the ion-momentum distributions [19,20]. While NSI proceeds through intermediate virtual states, SI is approximated as a "stepwise" absorption (see, e.g., [19]) involving intermediate stationary states, usually the ground states of the corresponding ions with increasing charge state for increasing numbers of photons absorbed. Hence, for SI typically more photons are required to reach the same final charge state as for NSI. Since the ionization yield should increase with the light intensity as $Y = \sigma_n I^n$ according to perturbation theory, where I is the intensity, σ_n the generalized n-photon cross-section and n the number of involved photons, NSI is predicted to dominate at low intensities, whereas the sequential mechanism takes over at higher intensities [21]. Measuring the ion yields for various channels as a function of the intensity the number of absorbed photons and, in certain cases, the nature of the absorption, SI or NSI, can be determined (see, e.g., [19]).

The potential curves for preferential decay channels as a function of internuclear distances and the measured KER spectra for coincident fragments $N^+ + N^+$ and $N^+ + N^{2+}$ are depicted in Fig. 1. According to and in agreement with previous assignments [11,12,15] mainly three dissociative states $A^1\Pi_u$, $d^3\Pi_g$, and $D^1\Sigma_u^+$ of N^{2+} can be attributed to the KER spectra peaked at about 6.6, 7.8, and 10.4 eV, respectively. In order to extract the number of absorbed photons for certain fragmentation pathways we have analyzed their intensity-dependent yields in Fig. 2. The ion yield is in arbitrary units. However, the relative intensities of the different fragmentation and ionization channels are correctly normalized with respect to each other.

We thus find that dissociative molecular dication production $N_2^{2+} \rightarrow N^+ + N^+$ as well as ground state N_2^{2+} ($X^1\Sigma_g^+$) formation are both dominated by two-photon absorption. While this can be easily understood for the dissociative states $A^1\Pi_u$, $d^3\Pi_g$, and $D^1\Sigma_u^+$ where most of them simply cannot be populated via one-photon absorption, this is definitively different for $X^1\Sigma_g^+$ (43 eV above the N_2 ground state) which is clearly in reach of one 44 eV photon. We interpret that as being due to exceedingly small cross sections close to the DI threshold. On the contrary, sequential two-photon DI involving, e.g., excited states of N_2^+ is expected to be relatively large such that we can state in general, that all dications apart from the $N^{2+} + N$ final channel are formed by SI via the ground or excited states of N_2^+.

Along these lines, it seems plausible that three-photon absorption dominates $N^{2+} + N$ production even though only two photons would be needed. Here, a one-photon absorption threshold for the $(1\gamma, 2e)$ reaction has been established recently at ~55 eV with a cross section of only $\sim 5 \times 10^{-21}$ cm^2 at $E_{\mathrm{exc}} \sim 10$ eV excess energy [10]. This excess energy is just about reachable with a second 44 eV photon in a $(2\gamma, 2e)$ process from the bound N_2^+ states or *F* band, predominantly populated via single-

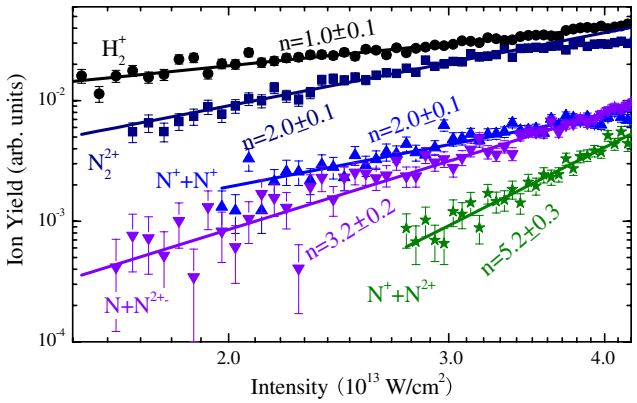

FIG. 2 (color online). Ion yields as a function of the laser intensity I. Solid points and solid lines denote the present measurements and fits ($\log Y = n \cdot \log I + \log \sigma_n$), respectively.

photon absorption [17], such that the cross section for the $(2\gamma, 2e)$ pathway is expected to be small as well and, accordingly, $(3\gamma, 2e)$ could take over.

Certainly surprising, however, is that as much as five photons within one light-pulse (~25 fs) need to be absorbed for the creation of N_2^{3+} ions, even though already two would be enough (NSI) relying on the potential curves given by Bandrauk [22]. Along the above argumentation one might immediately be convinced that $(2\gamma, 3e)$ has a tiny cross section only. But triply charged molecules could be easily created via sequential three- or four-photon absorption with quite comfortable excess energies of 47 eV and 91 eV, respectively, for the lowest $^2\Pi_u$ state leading to the $N^{2+}(^2P) + N^+(^3P)$ dissociation limit. Whereas in general this underlines the effectiveness of SI compared to NSI for multiple ionization (MI) of molecules, it is completely unclear why an excess of three photons as compared to the NSI and of two relative to the lowest-energetic SI channel dominate N_2^{3+} creation. Because of the absence of photoelectron spectra this question cannot be clarified in this Letter.

In Fig. 3 we present fragment-ion angular distributions (FIAD) differential in the KER for N^+, coincident $N^+ + N^+$ as well as N^{2+} ion emission, respectively. FIADs in Fig. 3(a) are predominantly due to *single-photon* single ionization, (γ, e), and can be partly compared to previous work. The peak located at $\cong 2$ eV corresponds to the dissociation channels $N_2^+(F^2\Sigma) \rightarrow N^+ + N$. Clearly, the F band of N_2^+ prefers to dissociate along the polarization $\hat{\varepsilon}$ axis, which agrees well with results of earlier measurements [23]. At 44 eV the photoionization cross section of N_2 into the H-band ($5^2\Sigma_g$ and $6^2\Sigma_g$), dissociating to $N^+ + N$ with KERs of about $7 \sim 8$ eV [17,24], is even larger than that into the F band [25] and the corresponding peaks are clearly seen. Both, F and H bands play a key role in the observed FIADs. They dissociate parallel to $\hat{\varepsilon}$ actually creating absorption alignment which will become important when $(2\gamma, 2e)$ is considered. Note that in these noncoincident data, N^+ ions emerging from N_2^{2+} $(2\gamma, 2e)$ Coulomb exploding to $N^+ + N^+$ might occur.

In order to clearly disentangle the latter contributions and to unambiguously shed light on *two-photon* DI of a molecule we analyze in Fig. 3(b) the $(N^+ + N^+)$ channels resulting purely from $(2\gamma, 2e)$ as proven by the intensity dependence in Fig. 2. In striking contrast to the single-photon absorption data as well as to results for $(1\gamma, 2e)$ after K-shell absorption [11] and $(n\gamma, 2e)$ *multiphoton* DI in optical laser fields [16], all exploding parallel to $\hat{\varepsilon}$, the dications from sequential $(2\gamma, 2e)$ are observed to predominantly fragment perpendicular to $\hat{\varepsilon}$ for the channels originating from N_2^{2+} in the $A^1\Pi_u$ (a) and $d^3\Pi_g$ (b) states whereas those originating from $D^1\Sigma_u$ (c) are mainly oriented along the polarization (note, events for $\theta < 20^\circ$ are removed because of the detector dead time).

This finding, along with the fact that the molecule cannot rotate by 90° within ~25 fs where SI occurs, allows us to (i) trace SI pathways and (ii) analyze photo-

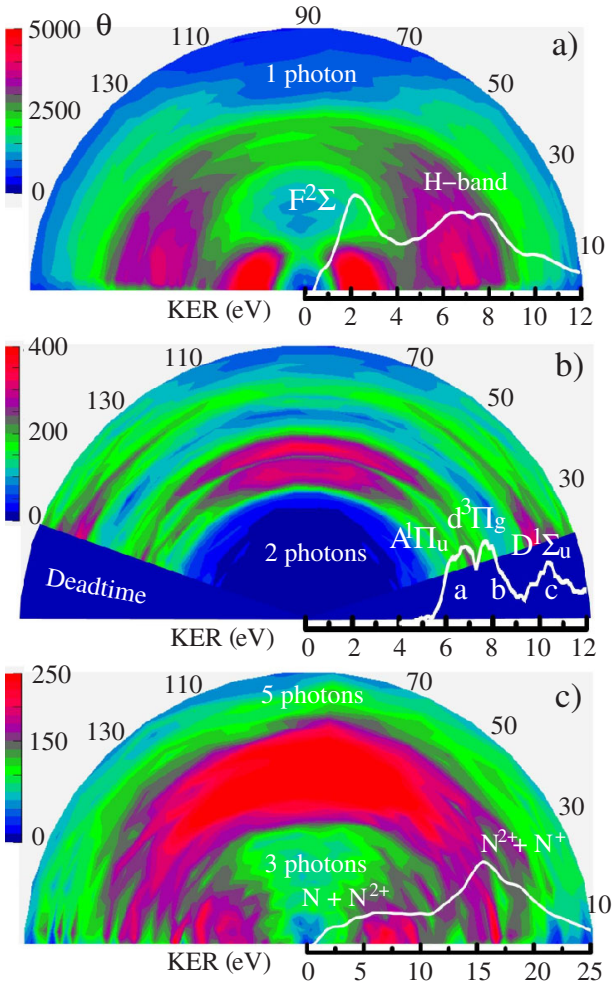

FIG. 3 (color online). FIAD polar density plots differential in the KER for various fragmentation channels. θ and the radius represent the angle with respect to the polarization axis (horizontal) of the linearly polarized light and the KERs, respectively. Curves display the KER spectra integrated over all fragment emission angles θ. (a) noncoincident N^+ fragments. (b) $N^+ + N^+$ coincidences. (c) noncoincident N^{2+} ions.

ionization from aligned molecular ions, never investigated before. Thus, there is strong evidence that the $A^1\Pi_u$ (a) and $d^3\Pi_g$ (b) states (perpendicular explosion) cannot be created via SI from the dissociating F and H bands (parallel dissociation), but rather should result predominantly from single-photon absorption from the bound N_2^+ states whose potential absorption alignment we cannot detect by our fragment-ion coincidence method.

Proceeding to noncoincident N^{2+} fragments in Fig. 3(c) and using the potential curve evaluated in Ref. [10] we can assign KERs below ~10 eV to the $(3\gamma, 2e)$ channel dissociating to the $N^{2+}(^2P) + N(^4S)$ limit. Since the fragmentation exclusively occurs parallel to $\hat{\varepsilon}$ a population through the F and H bands as well as possibly through the bound N_2^+ states (unknown alignment) are allowed. For the triply ionized final states instead, produced via absorption of not less than five photons (Fig. 2) and with KERs above

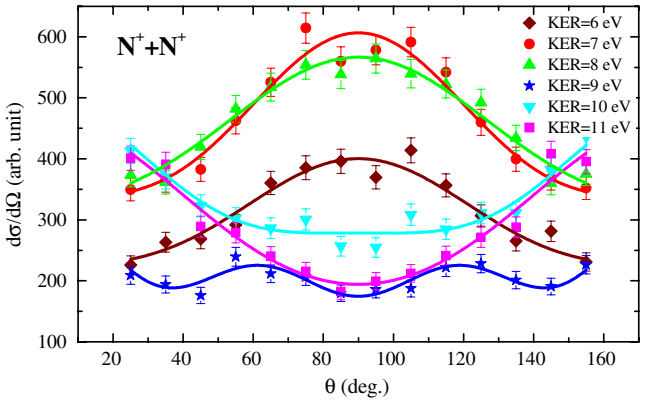

FIG. 4 (color online). FIADs for selected KER regimes (dissociation states).

$\sim$10 eV [outer part in Fig. 3(c)], we find exclusive $N^{2+} + N^+$ explosion along the perpendicular direction, essentially ruling out the N_2^+ (F and H bands) as well as the $N_2^{2+}(D^1\Sigma_u^+)$ state as intermediate sequential steps. Certainly, population through the singly ionized N_2^+ (bound), the ground and metastable states of N_2^{2+} (all with unknown absorption alignment) or via the perpendicular dissociating N_2^{2+} ($A^1\Pi_u^+$ and $d^3\Pi_g$) is allowed.

We finally present without further analysis in Fig. 4 angular distributions for selected $N^+ + N^+$ channels, characterized by their KERs as indicated in the figure, exhibiting a rich variety. We find perpendicular emission for KERs of 6, 7, and 8 eV but, now looking in detail, with indications of absorption enhanced alignment [26] at 7 eV. Also, parallel fragmentation exhibits different subtle patterns, e.g., for KERs of 10 and 11 eV. Even more complicated emission patterns pointing to higher-order contributions, for example, angular asymmetry parameter β_6, are observed at a KER around 9 eV. For few-photon absorption the FIADs can be characterized by a multiple expansion in terms of Legendre polynomial, $\frac{d\sigma}{d\Omega} = \frac{\sigma_0}{4\pi}(1 + \sum_{i=1,\cdots,n}^{n} \beta_{2i} P_{2i}(\cos\theta))$, where n are the number of absorbed photons and β_{2i} are anisotropy parameters.

In summary, few-photon induced multiple ionization and fragmentation of N_2 was explored. Inspecting the intensity-dependent yields we find that sequential ionization (SI) is the dominant, most effective multiphoton absorption pathway for molecules in the EUV regime. This is due to the large number of highly excited ionic states available being essentially stationary even for Coulomb-exploding levels on the $\sim$25 fs time scale of the FLASH pulses. We find the number of photons absorbed significantly exceeding the minimum number requested by the respective thresholds for some channels, a phenomenon that might only be partly explained by tiny multiple ionization cross sections close to thresholds. We observe rich-structured patterns in the KER-dependent FIADs highlighting alignment-dependent multiphoton absorption and ionization dynamics allowing us to trace SI pathways in details for some of the channels. Moreover, we provide evidence that photoionization of aligned molecular ions produced in earlier steps of SI via absorption alignment can be explored.

In the future it will be straight forward to record electron coincidences providing the exact characterization of the intermediate and final states, respectively. This technique is highly efficient for the investigation of photoionization of aligned and, most likely polarized molecular ions. Moreover, pump-probe experiments are presently under preparation bringing us in the position to directly access the dynamics of highly excited states.

Support from the Max-Planck Advanced Study Group at CFEL and from HGF "Virtual Institut Atomic and Cluster Physics at FEL" is gratefully acknowledged. Y. H. J. is grateful for support from DFG project no JI 110/2-1. We are greatly indebted to the scientific and technical team at FLASH, in particular, the machine operators and run coordinators, all together being the foundation of its outstanding performance.

[1] R. R. Meier, Space Sci. Rev. **58**, 1 (1991).
[2] D. J. Hollenbach and A. G. G. M. Tielens, Rev. Mod. Phys. **71**, 173 (1999).
[3] W. Ackermann *et al.*, Nat. Photon. **1**, 336 (2007).
[4] T. Shintake *et al.*, Nat. Photon. **2**, 555 (2008).
[5] H. B. Pedersen *et al.*, Phys. Rev. Lett. **98**, 223202 (2007).
[6] A. A. Sorokin *et al.*, J. Phys. B **39**, L299 (2006).
[7] A. Föhlisch *et al.*, Phys. Rev. A **76**, 013411 (2007).
[8] T. Sato *et al.*, Appl. Phys. Lett. **92**, 154103 (2008).
[9] T. Okino *et al.*, Chem. Phys. Lett. **432**, 68 (2006).
[10] P. Franceschi *et al.*, J. Chem. Phys. **126**, 134310 (2007).
[11] Th. Weber *et al.*, J. Phys. B **34**, 3669 (2001).
[12] M. Ahmad *et al.*, J. Phys. B **39**, 3599 (2006).
[13] B. Zimmermann *et al.*, Nature Phys. **4**, 649 (2008).
[14] M. S. Schöffler *et al.*, Science **320**, 920 (2008).
[15] M. Lundqvist *et al.*, J. Phys. B **29**, 1489 (1996).
[16] S. Voss *et al.*, J. Phys. B **37**, 4239 (2004).
[17] E. Gagnon *et al.*, Science **317**, 1374 (2007).
[18] J. Ullrich *et al.*, Rep. Prog. Phys. **66**, 1463 (2003).
[19] R. Moshammer *et al.*, Phys. Rev. Lett. **98**, 203001 (2007).
[20] A. Rudenko *et al.*, Phys. Rev. Lett. **101**, 073003 (2008).
[21] M. G. Makris and P. Lambropoulos, Phys. Rev. A **77**, 023401 (2008).
[22] A. D. Bandrauk, D. G. Musaev, and K. Morokuma, Phys. Rev. A **59**, 4309 (1999).
[23] J. H. D. Eland and E. J. Duerr, Chem. Phys. **229**, 13 (1998).
[24] T. Aoto *et al.*, J. Chem. Phys. **124**, 234306 (2006).
[25] S. Krummacher, V. Schmidt, and F. Wuilleumier, J. Phys. B **13**, 3993 (1980).
[26] R. N. Zare, Mol. Photochem. **4**, 1 (1972).
[27] R. W. Wetmore and R. K. Boyd, J. Chem. Phys. **86**, 5540 (1986).