Direct time resolved observation of molecular dynamics induced by soft-x-ray photoionization

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Abstract. We report the first direct observation of ultrafast dynamics in molecules induced by ionizing radiation. We use high harmonic upconversion process to generate soft-x-ray pulses of few femtoseconds duration, which photoionize N$_2$ molecule. This leads to the formation of highly excited N$_2^+$ ions via inner-shell ionization and electron shakeup processes. We time resolve the unexplored fragmentation dynamics of the electron shakeup states with femtosecond resolution using a strong-field IR probe. The IR pulse promotes the dissociating N$_2^+$ wavepacket to repulsive N$_2^{2+}$ potential. We obtain kinetic energy release of N$^+$/N$^+$ channel as function of time delay and observe a rapid transition from spherically-symmetric molecular potential to a two-center potential within ~150 fs.

1. Introduction

A pervasive theme in ultrafast science is to understand and control dynamics in atoms and molecules by employing ultrashort light pulses as a “strobe” to stop motion[1]. Multiphoton techniques are used extensively for femtosecond-resolution studies of atomic and molecular dynamics[2]. However, multiphoton excitation of a molecule is incapable of directly and cleanly ionizing inner-valence/core levels. X-rays can be used to excite and ionize inner electrons; however, to date x-ray sources have not had the femtosecond pulse duration necessary to directly observe radiation-induced dynamics. Fourth-generation sources such as free electron x-ray lasers are currently being developed in part to make such studies possible.

Fortunately, laser-generated high-order harmonics can provide such a source with unique capabilities for probing highly-excited dynamics[3]. To date, a number of studies have used high harmonics to probe dynamics in atoms molecules and surfaces. In recent work [4], a soft x-ray pulse was used to inner-shell ionize a xenon atom. The resultant Auger decay lifetimes were then measured and shown to be in agreement with spectral measurements. In molecular systems however, x-ray ionization can initiate complex dynamics that is much less understood than in atoms, and that involves many excited and correlated electron channels that cannot be easily calculated. Therefore, time-resolved measurements of x-ray driven dynamics in molecules can play a critical role in developing new understanding. However, to our knowledge, none of the studies so far have used an ultrafast soft-
x-ray source as an ionizing pump to initiate the molecular dynamics. Here we discuss our recent work[5] which represents the first femtosecond time-resolved experiment to use ultrafast soft-x-ray light as the pump source, to obtain real-time information on previously unexplored dynamics of shakeup states in the N$_2$ molecule. We accomplished this using efficient phase-matched soft-x-ray high-harmonic generation, and coincident 3-dimensional photofragment momentum reconstruction techniques[6].

2. Experimental

High harmonic light is generated in a phase-matched geometry[7] by upshifting intense 2 mJ, 800 nm, 28 fs, pulses from a 2 kHz ultrafast Ti:sapphire laser system (KMLabs, Inc.) in a 2.5 cm long 150 µm diameter, hollow waveguide filled with Ar gas. The peak laser intensity in the waveguide is $\sim10^{14}$ W cm$^{-2}$, and the argon pressure is $\sim$30 torr. A single harmonic from the comb of odd harmonics emerging from the waveguide is selected using multilayer optics, and focused to $\sim$100 µm spot using two mirrors in a z-fold configuration. This results in a 43 eV pump beam, with a pulse duration of $\approx 5$ fs, and with a flux of $\approx 10^6$ photons/pulse or $2 \times 10^9$ photons/sec. Part of the laser output is split, delayed, and then recombined with the pump beam to serve as a collinear probe beam. The probe beam is focused using a 75 cm lens to a $\sim$100 µm diameter spot with intensity $\sim 10^{12} - 10^{13}$ W cm$^{-2}$. The target gas is cooled in a supersonic jet expansion, and the cold supersonic part of the jet selected using a skimmer. The molecular gas density in the interaction region is estimated to be $10^{11}$ cm$^{-3}$. After the interaction region, the supersonic jet enters a differentially pumped region, thus maintaining low background pressure in the main interaction chamber. This experimental setup was run continuously with excellent stability and minimal loss in detector count rate for data runs > 100 hours duration.

![Experimental setup](image)

**Figure 1.** Experimental set up. (a) High harmonic generation in a Ar gas filled waveguide is used to upconvert IR photons to soft-x-ray regime. Soft-x-ray pulses are used as pump for excitation, and a part of IR pulse serves as probe. (b) Soft-x-ray spectrum after energy filtering with multilayer mirrors. (c) Reaction microscope consisting of uniform electric and magnetic fields for guiding interaction fragments. Time of flight and position information from delay line anodes and is used to reconstruct 3-dimensional momentum of electrons and ions in coincidence.
The reaction microscope consists of an electrode configuration that generates a uniform electric field in the interaction region, to accelerate reaction fragments toward the detectors. A magnetic field is also used to confine the fast-moving electrons. The result is near-4\pi collection efficiency for both electrons and ions. The fragments are then detected by microchannel plates employing a position-sensitive delay line anode (Roentdek, Gmbh). These detectors record the detection coordinates and time-of-flight of the fragments with spatial and temporal resolution of \( \sim 100 \mu \text{m} \) and 500 ps respectively. This information, together with knowledge of the initial position (defined by the interaction region) and the electric and magnetic fields, enables reconstruction of all three components of momentum of each particle that hits a detector. Using this reaction imaging apparatus, electron and ion data are accumulated for each laser shot. Post analysis of the data is then used to deduce electron-ion correlations and to implement coincidence conditions that filter the data to identify the different dissociation channels.

3. Results and Discussion

Figure 2. Electron and ion energy of fragments obtained in coincidence using reaction microscope when soft-x-ray pulse is used to pump and excite \( \text{N}_2 \) molecules. The diagonal feature labelled \( n=3 \) corresponds to the set of correlated fragmentation events corresponding to highly excited shake-up states.

Photoionization of the \( \text{N}_2 \) molecule with soft-x-ray light can initiate a series of complex dynamics. The ground state configuration of \( \text{N}_2 \) is \( 1\sigma_g^21\sigma_u^22\sigma_g^22\sigma_u^21\pi_u^43\sigma_g^2 \) and a 43 eV photon can remove both outer-valence (\( 3\sigma_g^51\pi_u^4 \)) and inner-valence (\( 2\sigma_g^52\sigma_u^2 \)) electrons. The inner-valence ionization pathway results in the formation of many highly excited ion states (\( \text{N}_2^{+*} \)), with potential energies between 23 and 43 eV (relative to the \( \text{N}_2 \) ground state) [8]. The cross sections for forming these states are known from synchrotron measurements[8]. The finite bandwidth of our photon source does not allow us to resolve each state separately; however, previous work[8-11] indicates that most of these inner valence ionized molecules rapidly evolve to separated \( \text{N}(2s^22p^3) \) and \( \text{N}^+(2s^22p^2) \) fragments, i.e. electronic states with principle quantum number \( n=2 \). However using the reaction microscope, we observe a very significant fraction of dissociation events that cannot be explained purely by dissociation of inner-valence hole states as shown between black lines in Fig. 2. These events represent low energy ion hits correlated with low energy electron. The energy conservation equation \( E_{e^-} + 2E_{N^+} = h\nu - E_{\text{limit}} \) indicates that such channels represent a molecular excitation near the double ionization threshold (~ 43 eV) that dissociates to a ground state ion and an excited neutral atom, with the outer electron in an \( n=3 \) principle quantum number state. These pathways have not been investigated previously. We show below that these dissociation channels are consistent with fragmentation of excited states resulting from an electron shakeup process accompanying outer valence \( 3\sigma_g \) ionization.
Figure 3. (a) The pump soft-x-ray pulse photoionizes N\textsubscript{2} to a highly excited dissociative state. The probe IR pulse further ionizes the ion to the final di-cation state. A schematic of the wave function for the N\textsubscript{2}\textsuperscript{+*} state is shown at different internuclear separations. (b) Evolution of the ion kinetic energy release in the N\textsuperscript{+}/N\textsuperscript{+} channel as function of time delay between the soft-x-ray pump pulse and the IR probe pulse. Theoretically calculated KER using the 4\textsigma\textsubscript{u} electron is shown overlaid in black lines.

In order to study the dynamics of soft-x-ray pumped highly excited states near double ionization threshold, we use a time delayed probe IR pulse. The IR pulse multiphoton ionizes the evolving N\textsubscript{2}\textsuperscript{+*} wave packet and promotes it to ground state of N\textsubscript{2}\textsuperscript{2+}. This is repeated at various time delays between pump and probe pulses in small steps, thus interrupting the N\textsubscript{2}\textsuperscript{+*} wavepacket at various stages of dissociation. This pump-probe scheme is shown in figure 3(a) along with representations of potential energy curves for highly excited state N\textsubscript{2}\textsuperscript{+*} and final N\textsubscript{2}\textsuperscript{2+} state as E\textsubscript{1}(r) and E\textsubscript{2}(r). The resultant doubly ionized N\textsubscript{2}\textsuperscript{2+} explodes into two N\textsuperscript{+} ions which are correlated in momentum. Using reaction microscope we isolate coincident N\textsuperscript{+} ions hits with almost equal and opposite momentum. The kinetic energy release (KER) in the coincident channel is shown as a function of time delay is shown in figure 3(b). This time resolved KER data shows interesting behavior. There is fast decrease from 7 eV to 4 eV within 150 fs and then a slow decay. In order to quantitatively understand this behaviour we performed theoretical calculations and compared them with experimental results.
We theoretically construct states to correspond approximately to a doubly ionized ground-state (N$_2^{2+}$) molecular core with an additional excited electron. We calculated the effective potential of N$_2^{2+}$ ions in the ground state by the multiple-scattering self-consistent method[12]. The orbital energy of various excited shakeup states was calculated using an effective potential with a Coulomb tail correction in the asymptotic region. Adding this orbital energy to the ground state energy of N$_2^{2+}$, we obtained the potential-energy curves for the excited shakeup states (Fig. 4). These states are populated when the electron in a 3$\sigma_g$ state is ejected by a 43-eV photon, and a second valence 3$\sigma_u$ electron is promoted to the higher valence levels 3$\sigma_u$, 4$\sigma_u$, 4$\sigma_g$, and assorted $\pi$ orbitals. The electron state corresponding to a 4$\sigma_u$ shakeup (black solid squares curve in Fig. 4) is closest to the N$_2^{2+}$ ground state and has the largest overlap with the valence 3$\sigma_g$ orbital. Hence, this state is most likely to be populated in the Frank-Condon region as a result of an electron shakeup process. This state then decays to the dissociation limit, with the final configuration of fragments corresponding to an ion N$^+$ ($^3P$) and a neutral N atom ($n = 3$). We chose this electron state corresponding to 4$\sigma_u$ shakeup (Fig. 4) as a likely candidate for $E_1(r)$ in Fig. 3(a). Similarly using the known final N$_2^{2+}$ state from the previous work[13] for $E_2(r)$ in Fig 2(a), we calculated the KER at different stages of fragmentation. The kinetic energy release at any given time delay $t$ between the soft-x-ray pump and the IR probe is determined by the sum of the energy that the ions gain on the N$_2^{2+}$ state (times $t \rightarrow t$), as they evolve from the Frank-Condon region towards the dissociation limit, plus the energy gained after time $t$ on the known N$_2^{2+}$ dissociation curve[13]. The KER and the internuclear distance as a function of time delay is represented by the following classical equations:

$$KER(t) = [E_1(r_0) - E_1(r_t)] + [E_2(r_0) - E_2(\infty)]$$

(1)

$$dr_i / dt = \sqrt{2(E_i(r_0) - E_i(r_t)) / \mu}$$

(2)

Here $\mu$ is the reduced mass and $r_0$ and $r_t$ are the internuclear distances at times 0 and $t$ respectively.

The theoretically calculated KER is plotted in figure 3(b), overlaid on experimental data in the form of two black lines. The width of this band arises from the width of wave-packet at time zero in the Frank-Condon region and the exact nature of potential well of the excited and final states. The
important thing to note is the excellent agreement between the experimental and theoretical data, indicating that most of the fragmentation is resulting from a state corresponding to 4σ_u shakeup.

We interpret this KER evolution in terms of the dynamics of N_2^+* molecular wave function corresponding to antibonding 4σ_u orbital. Fig 3(a) also shows the 4σ_u orbital at different states of evolution. Near time-zero, the interatomic distance is small, with no electron density between the two nuclei. This results in the large observed KER. In this situation, the electron experiences almost spherically symmetric molecular potential. As internuclear distance increase, the system goes through a transition region where the internuclear distance is comparable to the electron shell radius. In this case the electron density between two nuclei becomes substantial, effectively reducing the observed KER. This situation corresponds to distinct two-center molecular potential. Finally, we observe a flat KER that implies loss of long range Coulomb interaction, which is certainly expected since one of the partners is neutral.

4. Conclusion and Acknowledgements

In conclusion, using a femtosecond soft-x-ray pulse and an IR probe pulse, we map-out in real time the evolution of highly excited molecular shakeup states. We observe excellent agreement between experiment and theory motivated by this work. This work is to our knowledge the first to use soft-x-ray light generated from high harmonics to study previously-unknown dynamics of a process that occurs in nature, and that could not be accessed using more-conventional techniques.

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5. References

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