

Time-resolved X-ray spectroscopy for X-ray-induced phenomena

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ABSTRACT

X-ray-pump/x-ray-probe spectroscopy allows investigation of ultrafast x-ray induced molecular dynamics. X-ray absorption and Auger decay leave molecules in manifolds of transient intermediate states in the femtosecond time scale. By using an x-ray probe pulse, we can image nuclear wavepackets as a function of time using ion-ion coincidence spectroscopy to record ion momentum distributions and kinetic energy releases (KERs). Numerical simulations, a time-dependent approach that includes both K-shell photoionization and Auger decay, show how the transient intermediate states are projected onto the KERs. At short time delays, the measurements are sensitive to interatomic interactions, whereas at longer delays the contribution from separated ions due to dissociative intermediate states becomes observable. We present simulations for the nitrogen molecule. These simulations have the potential to be extended to more complex molecules.

Keywords: X-ray induced phenomena, ultrafast physics, *ab-initio* numerical simulations, time-dependent Schrödinger equation

1. INTRODUCTION

X rays have been a very powerful resource for spectroscopic applications due to their site specificity, i.e. the x-ray photon is absorbed in a particular atomic site of the system. This feature makes x rays the ultimate spectroscopic tool to look at a particular site of a physical system and retrieve both electronic and structural information. The impact and applications of x-ray spectroscopy techniques cover a wide range of fields such as Biology, Chemistry, and Physics.

New capabilities of XUV/x-ray sources are continuously being developed. On one hand, it is possible to generate very short pulses, one hundred attoseconds to a few femtoseconds, in the XUV and soft-x-ray regime by using strong-field lasers via the well-known nonperturbative process of high-harmonic generation (HHG). On the other hand, x-ray free-electron lasers (XFELs) deliver high-intensity x-ray femtosecond pulses, and recent self-seeding techniques have significantly improved their temporal coherence. Even new advances will push XFEL pulses into the attosecond regime. The development of these tools enable looking into the fastest processes in atoms, molecules, and condensed matter systems, and get a further insight of the underlying mechanisms in the first steps of any physical process and chemical reaction.

It is possible, both in XFELs and HHG sources, to produce two-color few-femtosecond x-ray/XUV pulses with controlled time delay. These capabilities enable the possibility of providing promising femtosecond x-ray spectroscopy tools to study precisely the x-ray interactions of ultrashort pulses^{1,2}. We have the unique opportunity to study those first fundamental processes triggered by x-ray photons, which are well-localized at a particular site of the physical system. Photoinduced dynamics initiated by the absorption of x rays are fundamentally very different than the dynamics initiated by the absorption of optical photons. Not only x-ray photons are absorbed in one site of the molecule, but also strong electron-electron correlations and nuclear relaxations constitute an intricate interplay. After excitation, charge transfer processes take place causing interesting x-ray-induced phenomena^{3,4}, such as isomerization⁵, bond breaking in another site of the molecule, or ultrafast spin-state dynamics in transition-metal complexes⁶. X-ray induced phenomena have been largely studied in synchrotrons. However, only access to the final products (photons, electrons, and ions) is possible, and our knowledge is limited to the modeling of those final states. It would be desirable to obtain also

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information of the intermediate transient states in order to get a better insight of the underlying mechanisms. These processes involve electron and nuclear motion, and it is critical to understand the first steps after excitation. Also, understanding these first steps also open the door to control the dynamics by using two-color few-femtosecond x-ray/XUV pulse^{7,8,9}.

In this work we present a technique to image the nuclear wavepackets of a diatomic molecule after x-ray excitation, by using two few-femtosecond x-ray pulses. This technique is suitable for experiments in which ions and electrons are measured in coincidence. In the following we present ab-initio simulations for an x-ray-pump -- x-ray-probe experiment in a nitrogen molecule².

2. IMAGING MOLECULAR NUCLEAR WAVEPACKETS

In the general case, absorption of an x ray by the molecule creates a core-hole state by the promotion of an inner-shell electron into a valence-like state or into the continuum. The core-hole state is highly unstable and decays rapidly, with a lifetime between hundreds of attoseconds to a few femtoseconds. The decay occurs either by nonradiative processes, such as Auger decay, or by radiative processes, such as x-ray fluorescence. The decay of the core-hole may induce other inner-shell or valence-shell holes in higher energy shells, consequently triggering other nonradiative or radiative processes. This picture is far more complicated in molecules than in atoms, because the nuclear motion must also be considered. The removal of electrons during nonradiative processes may produce highly-charged states with strong dissociative behavior. In some cases, the nuclear dynamics cannot be neglected even during the characteristic core-hole lifetimes.

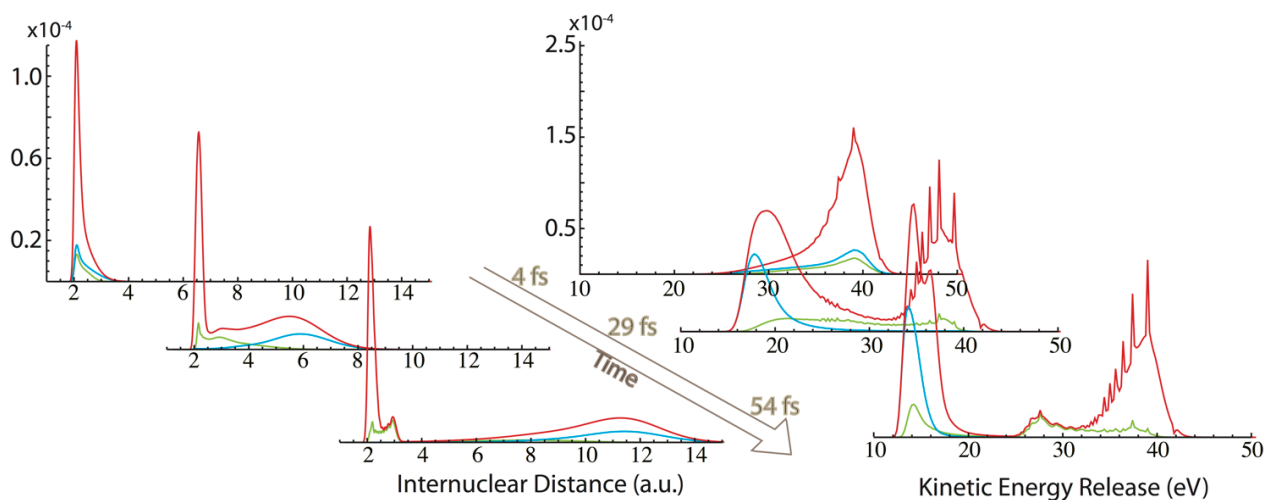


Figure 1. In the left figure, the nuclear wavepacket in the N^+-N^+ breakup channel at three different time delays. This channel is populated during the core-hole decay at the same time that nuclear wavepacket is evolving, considering thus the electron-nuclear coupling and all the interferences during the time evolution. In the right figure, the calculated KER for the N^+-N^{3+} when the probe pulse transfers population from N^+-N^+ to N^+-N^{3+} . Red line, when the first nine low-lying electronic states of the dication molecule are considered. Green line, only the $3\Pi_g$ electronic state is shown. Blue line, only the $1\Pi_g$ electronic state is shown.

In this work we present theoretical results in diatomic molecules based on a pump-probe scheme to study the fragmentation of the molecule upon the absorption of an x-ray photon. In molecules composed of low-Z elements, such as N_2 , the ionization of a K-shell electron creates a core-hole state in which the main decay is an Auger process involving two electrons in the valence shell. Therefore, after Auger decay, excited states with two holes in the valence shells are populated. On previous studies with femtosecond IR pump-probe lasers¹⁰, fragmentation of molecules was studied in which the molecules were strongly ionized and the ion fragments were detected in coincidence. By detecting the ions from highly-charged states, it was possible to infer information about the dynamics in the low-charged states. It was also demonstrated that by collecting the ions in coincidence at different time delays of the highly-charge breakup channels, and retrieving the kinetic energy release of the corresponding channel, one could infer from the quantum beats information about the vibrational states excited by the pump pulse and consequently information about the potential energy surface¹¹. Here we use a similar technique but the analogous one in the x-ray regime. In particular, we show how to gain information about the fragmentation of molecules with low-Z elements after the system response to the absorption of an x-ray photon. The main difference with the optical regime is that the excitation of a core electron strongly affects the other electrons, this produces several Auger processes in response to the strong correlation among electrons. The x-ray pump pulse will excite highly-excited states via those electron relaxation pathways.

In order to illustrate the potential of this technique and provide a clear example, we show first results for a simple molecule, N_2 . The core-hole lifetime in the nitrogen molecule is about 3.6 fs. An original theoretical approach was developed¹¹ in order to describe the K-shell ionization induced by the pump pulse and the Auger decay that populates a manifold of final dication states in a time-dependent framework, concurrently also with the time evolution of the nuclear wavepackets. This powerful approach allowed us to map quantum mechanical properties of the nuclear wavepacket in the N^+-N^+ channel into the N^+-N^{3+} via the K-shell ionization of the probe pulse, as illustrated in Fig. 1. We use Fourier-transform limited pulses with FWHM of 10 fs for the theoretical simulations. The bandwidths of the pulses are not relevant in this case, because the x-ray energies are far above the K-shell ionization threshold, so only core-hole states with a high-energy photoelectron are produced. The pump pulse ionizes the 1s orbital electron, and the excited nuclear wavepacket starts to move in the potential energy surface of the electronic core-hole state. During nuclear propagation, the core-hole state also decays by Auger transitions, mostly populating excited states of the dication molecule, as one additional electron -the so-called Auger electron- is emitted during this decay. There are several Auger transitions, but the main final dication states dissociates into the N^+-N^+ channel. In the left part of Fig. 1, the nuclear wavepacket is plotted in the N^+-N^+ breakup channel at three different time delays. By absorbing a second x-ray from the probe pulse, a second 1s electron from one atomic site is removed, and that triggers a second Auger process. The probe-induced K-shell ionization and Auger decay predominantly increases the charge state of the system by 2. Therefore, the nuclear wavepackets propagating in the dication states are promoted into tetracation states. At short internuclear distances, the valence electrons are delocalized and interatomic interactions are strong. There, the probe-induced Auger decay populates either the $N^{2+}-N^{2+}$ or the N^+-N^{3+} channel. As the separation between the ions increases, however, the probe interacts with an isolated N^+ ion and enhances the N^+-N^{3+} channel. Here we focus only on the N^+-N^{3+} breakup channel. The KER is an observable sensitive to the nuclear geometry of the molecule. If we assume that after probe excitation the nuclear wavepacket is promoted into a potential energy curve that is dominated by the Coulomb repulsion of the N^+ and N^{3+} ions, then the measurement of the KER of the N^+-N^{3+} breakup channel provides information of the nuclear geometry during probe excitation. Hence, by changing the time delay and measuring the KER, we can retrieve nuclear motion information of the low-charge-state channels, in this particular case of the N^+-N^+ channel. In the right part of Fig. 1, red line, we show the KER of all electronic states dissociating into the N^+-N^+ channel that have been promoted into the N^+-N^{3+} channel by the probe pulse. This shows the large amount of information we can obtain about the nuclear wavepacket by detecting the KER of N^+-N^{3+} at different time delays. Interestingly, the nuclear wavepacket is formed of dissociative states and quasi-bound states that, by "nuclear" tunneling, will end up dissociating. In Fig. 1 we also show the calculated KER from two specific electronic states, $1\Pi_g$ and $3\Pi_g$, that in principle we could obtain in an experiment in which the Auger electron is measured in coincidence with the ion fragments.

This technique based on a X-ray-pump/x-ray-probe spectroscopy is ideal for the new capabilities at XFELs of generating two femtosecond x-ray pulses. Ion-ion momentum coincidence measurements allow the retrieval of all ionic fragments of the system. This is a powerful measurement sensitive to the nuclear geometry. Using the second x-ray pulse we have shown that we are able to take a snapshot of the nuclear structure, whose time resolution is limited by the pulse length of

the probe pulse and the characteristic lifetime of the probe-induced Auger decay. New developments at XFELs are pushing towards pulses shorter than the natural lifetime of Auger decay. With such pulses, and a good theoretical modeling of the dynamics of our molecule that considers the Auger decay induced by the probe pulse, one could obtain a sub-femtosecond resolution.

3. CONCLUSION AND PERSPECTIVES

By using two x-ray pulses we can study molecular nuclear dynamics triggered by the absorption of an x-ray photon with femtosecond resolution. A first x-ray pulse is absorbed by the molecule and initiates the transient dynamics. Then a second x-ray pulse probes the molecular dynamics at variable time delays. The pump and probe pulses may have similar photon energies tuned well-above the K-shell ionization threshold. Here we have shown theoretical simulations of this technique by studying the molecular fragmentation of the nitrogen molecule. The probe-induced Auger decay maps the time-dependent nuclear wavepacket in a particular charge-state channel onto the Coulombic repulsive potential curve corresponding to a higher-charge-state channel, resulting in a delay-dependent KER. Hence, by measuring KERs at different time delays, we are able to resolve femtosecond nuclear dynamics in a specific breakup channel. This scheme fully exploits the recent capabilities at XFELs in order to generate two femtosecond x-ray pulses with controlled time delay, and it is not affected by the temporal or the energy jitter of the pulses, ideal for SASE pulses.

The presented quantum-mechanical simulations on nitrogen can be extended to more complex molecules. This work opens the possibility of designing time-resolved experiments with two x-ray pulses based on KER spectroscopy and study non-adiabatic effects and isomerization reactions. Also, future XFEL machines that will deliver pulses with high repetition rate will make possible experiments in which the ions are detected in coincidence with the electrons. By detecting the Auger electron the retrieval of the nuclear dynamics in a specific electronic state is possible. We could obtain a distribution in KER at different electronic states, as shown in Fig. 1, and obtain a complete picture of the electron and nuclear dynamics. This technique holds a great potential to disentangle the correlation and energy sharing between the electron and nuclear motion during isomerization reactions.

Also, future capabilities with much shorter pulses will enable the possibility to explore the nuclear wavepacket propagation during the same time scale as Auger processes. This might open the possibility to explore the role of Auger processes on the coherent evolution of the nuclear wavepackets.

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