



Ultrafast molecular dynamics illuminated with synchrotron radiation



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ABSTRACT

Synchrotron radiation is a powerful tool for studying molecular dynamics in small molecules in spite of the absence of natural matching between the X-ray pulse duration and the time scale of nuclear motion. Promoting core level electrons to unoccupied molecular orbitals simultaneously initiates two ultrafast processes, nuclear dynamics on the potential energy surfaces of the highly excited neutral intermediate state of the molecule on the one hand and an ultrafast electronic decay of the intermediate excited state to a cationic final state, characterized by a core hole lifetime. The similar time scales of these processes enable core excited pump-probe-type experiments to be performed with long duration X-ray pulses from a synchrotron source. Recent results obtained at the PLIEADES beamline concerning ultrafast dissociation of core excited states and molecular potential energy curve mapping facilitated by changes in the geometry of the short-lived intermediate core excited state are reviewed. High brightness X-ray beams combined with state-of-the-art electron and ion-electron coincidence spectrometers and highly sophisticated theoretical methods are required to conduct these experiments and to achieve a full understanding of the experimental results.

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1. Introduction

Molecular dynamics occur on a wide range of timescales spanning attoseconds to many seconds or even longer depending upon the processes involved. Typically, however, when discussing molecular dynamics of isolated molecules in the context of light-matter interactions, it is the motion of nuclei within the molecule, which occurs on the femtosecond ultrafast time-scale that is of interest. A pump-probe experiment to probe these molecular dynamics therefore requires femtosecond pulse durations and equivalent relative timing to be useful in the study of such processes. In order to interact with site-selected species in molecules through core-level excitation and ionization X-rays are a powerful tool to probe molecular dynamics using the well-established techniques of photoelectron, photoion and various particle and photon coincidence techniques. Synchrotron radiation is a common source of X-ray radiation and modern 3rd generation high-brightness storage rings typically have pulse durations on the order of 10s of ps, however, with repetition rates in the MHz to 500 MHz range, both

too long to follow this type of molecular dynamics and at too high a repetition rate for high powered pump lasers to be synchronized on a pulse-by-pulse basis. Recently developed X-ray free electron lasers provide both short wavelengths and short pulse-durations [1–3] and are suitable for pump-probe experiments [4,5], but access to these sources is limited and, as shown below, not always necessary to access molecular dynamics in some small molecules. In spite of the mismatch between the time scales of ultrafast dynamics and synchrotron radiation pulse durations, extensive use has been made of X-rays from synchrotrons to study molecular dynamic processes. Several extensive reviews of the phenomena involved and recent advances have been published recently [6–8] and only an outline of the mechanisms involved are given below.

Nature provides an inherent pump-probe mechanism in the form of core level excitation to empty molecular orbitals below the ionization continuum as illustrated in Fig. 1. Upon excitation of a core electron from the ground state of the molecule to a core excited state, consisting of a molecular orbital below the ionization potential, a competition between two temporal processes is launched. The energetic core-hole state is highly unstable and will decay with a lifetime typically on the order of a few femtoseconds. The excited electron, populating a molecular orbital that was previously not occupied, changes the nature of the bonding in the molecule. Depending on the nature of the unoccupied molecular

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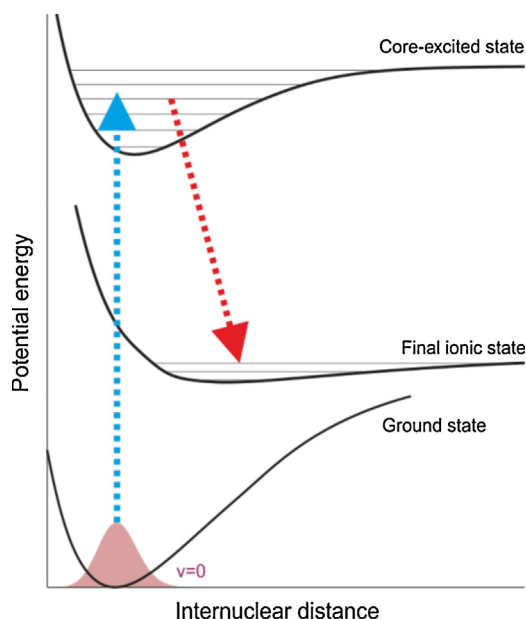


Fig. 1. Schematic representation of the potential energy curves for the initial ground state, intermediate core excited state and final cationic state with arrows indicating the excitation and deexcitation processes.

orbital a variety of dynamical process can be triggered. Unoccupied molecular orbitals can be antibonding orbitals and promotion of a core electron to this type of orbital initiates a dissociation of the molecule that begins immediately upon excitation of the electron. Empty molecular orbitals can also be bonding or non-bonding, inducing changes in the nuclear geometry, such as lengthening or shortening of the equilibrium bond length. Regardless of their bonding character, however, promotion of an electron from a core level to an empty molecular orbital launches nuclear dynamics in the molecule that occur on the ultrafast time scale of nuclear motion in molecules, femtoseconds.

The subsequent deexcitation of the core excited state to a more energetically favorable valence hole cationic state can be accomplished through Auger decay with ejection of an electron carrying away the excess energy of the transition. The Auger decay projects the electronic state of the molecule from the intermediate core excited state onto the potential energy surface of the final ionic state, which is often one of the manifold of lower ionic states (i.e. valence ionic states) of the molecule. The creation of holes in the valence shell of a molecule via the excitation of a core level electron to an empty molecular orbital is known as resonant photoemission and is a useful tool in studying ultrafast molecular dynamics.

As will be seen below, resonant photoemission provides exceptional detail about the nature of molecular potentials and dynamics when vibrational resolution of the final states is achieved. Observation of the vibration levels of the final cationic state provides a detailed probe of the nuclear dynamics by mapping the changes in the geometry upon excitation and deexcitation in the resonant photoemission process. State-of-the-art synchrotron sources, X-ray beamlines and electron spectrometers are required to achieve the required resolution at the high photon energies used to excite core level electrons. The PLEIADES beamline [9] at synchrotron SOLEIL where much of the work reported here was done is one such facility. The beamline covers the energy range from 7 to 1000 eV providing linearly and circularly polarized light with high brightness and spectral resolution. End-stations for high-resolution electron spectroscopy and electron-ion coincidence spectroscopy designed for studying dilute gaseous samples were used for several of the studies reported here.

Interpretation of the experimental data to extract the underlying physical processes involved requires equally sophisticated theoretical methods. Recent developments in modeling core level excited states and their decay to cations final states involve high level ab initio computation of molecular potentials, time dependent nuclear dynamics and excitation and deexcitation probabilities. The intricacies of these exquisite theoretical methods are not discussed in the following discussion, but their results have been essential in interpreting the experiment spectra. Readers are directed to the original source materials referenced below for details on the theoretical methods.

A selection of examples have been chosen from recently reported studies from the PLEIADES beamline at Synchrotron SOLEIL to illustrate how high-resolution synchrotron radiation can be used both to study and capitalize on molecular dynamics in small molecules. Ultrafast dissociation, where core excitation initiates the fragmentation of a molecular bond is both discussed from a fundamental viewpoint and used as a tool to view new physics in these examples. High resolution resonant photoemission is demonstrated as a tool for investigation of the dynamics in core excited molecules and an illustration of how it can be used to study otherwise inaccessible valence ionization states of molecules is presented. Overall, in spite of the mismatch of the pulse duration of X-rays from synchrotron with nuclear dynamic processes in small isolated molecules these results illustrate that the use of state-of-the-art experimental synchrotron X-ray sources and beamlines, electron and coincidence spectrometers and recently developed theoretical methods provides a means to study these processes in extraordinary detail.

2. Ultrafast dissociation

Ultrafast dissociation following excitation of a core electron to an antibonding molecular orbital was first identified in the molecule HBr in 1986 [10] following excitation of Br 3d electrons to the σ^* resonance at 70.6 eV. The molecule was chosen as an iso-electronic molecular analog of Kr where previous studies of Auger spectra of resonantly excited core level states had identified numerous new lines corresponding to Auger decays in which the excited electron participated in the decay or remained in an excited state as a spectator to the process [11]. Rather than observing the expected broad feature in the spectrum of HBr, however, a set of sharp lines were found and identified as resulting from Auger decay of atomic Br. The atomic lines were unambiguously identified when they were found to maintain a constant kinetic energy when the photon energy was changed as shown in Fig. 2.

A model of rapid dissociation of the molecule before the core hole lifetime limited Auger decay of the Br 3d core hole caused by the excitation of the Br 3d electrons onto the dissociative potential energy curves of the σ^* state has been suggested, as illustrated in Fig. 3. In this explanation of the surprising observation of atomic Br resonant Auger lines following core level excitation of HBr, excess energy from the projection of the electron distribution onto the dissociative curves is carried away as kinetic energy of the fragment atoms and the electron energies are determined solely by transitions between the atomic energy levels in the Br atom. Subsequent studies of the analogous CH₃Br molecule found similar atomic Auger lines but with reduced relative intensity compared to those found in HBr [12], attributed to the increased mass of the CH₃ moiety, versus H, separating from the Br atom, and hence reduced speed and lesser internuclear separation at the instant of Auger decay or the Br 3d core hole.

Ultrafast dissociation in HBr and its manifestations in electron spectroscopy continues to be an active area of research. A detailed study of electron emission from HBr in the vicinity of the σ^*

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