X-ray–Ion Coincidence Spectroscopy of Atoms and Molecules

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Introduction

Atomic x-ray absorption typically excites or ejects a deep inner-shell electron, producing a vacancy state that relaxes by a series of radiative (x-ray fluorescence) and radiationless (Auger-electron emission) processes. K-shell vacancies in high-Z atoms decay preferentially by K-L x-ray fluorescence in which the vacancy is transferred to the L shell. In lower-Z atoms, K vacancies decay preferentially by a K-LL Auger process in which a second electron is ejected and two vacancies are produced in the L shell. The fluorescence yields of L vacancies also depend strongly on Z, but are more likely than K vacancies to decay by an Auger process, e.g., L-MM, producing multiple vacancies in the M shell. Radiationless processes become increasingly dominant as vacancies are transferred to outer shells, with the result that several valence-shell electrons are removed in the final state. A wide range of final charge states are produced due to alternative decay pathways.[1] If the initial K vacancy is produced in a high-Z atomic constituent of a molecule, a similar vacancy cascade occurs, but removal of delocalized valence electrons produces positive charge on two or more atomic centers and results in ion fragmentation (Coulomb explosion). If the K vacancy is produced in condensed matter, the emitted photons and electrons can produce secondary excitation or ionization of neighboring atoms. For example, optical luminescence is observed from rare-earth materials following x-ray absorption.[2]

Coincidence techniques, in which two or more ejected photons, ions, or electrons are detected simultaneously, allow specific decay pathways to be selected from a complex vacancy-cascade process. We have previously studied the decay of K vacancies in atomic Ar by recording ion charge-state yields in coincidence with Auger electrons[3] and by recording Auger-electron spectra in coincidence with x-ray fluorescence.[4] By tuning the incident x-ray energy through the absorption edge, the inner-shell electron is excited to bound and continuum states near threshold, where the excitation and decay processes are coupled and must be treated as a one-step scattering process.[3] In the present experiments, atomic or molecular ions were detected in coincidence with fluorescent x-rays. Ion charge-state yields of Kr and Xe were measured across their respective K edges at 14.3 and 34.6 keV. We also studied ion fragmentation of $CBrF_3$ following x-ray absorption at the Br K edge (13.5 keV). Information on fragment-ion correlations was obtained by detecting two ions in coincidence with the same x-ray.

Methods

Measurements were made on the BESSRC-CAT bending-magnet (12-BM), undulator (12-ID), and wiggler (11-ID-D) beamlines. The incident x-ray beam passed through an effusive gas jet positioned between the extraction grids of a time-of-flight (TOF) ion spectrometer. An x-ray detector positioned opposite the TOF spectrometer detected fluorescent x-rays. X-rays are detected promptly while ions are detected after a time delay that depends on the mass (m) and charge state (q) of the ion. Initial measurements were made with an avalanche photodiode (APD) with sufficient time resolution (< 1 ns) to record ion TOF spectra with good m/q resolution. In recent experiments, the APD was replaced with a Si(Li) detector, which allowed ion TOF spectra to be recorded in coincidence with specific fluorescence transitions. To overcome the limited time resolution of the Si(Li) detector (≈ 20 ns), detected x-rays and ions were both referenced to the rf bunch marker, which is temporally well defined (< 1 ns). While a single ion is detected from atomic targets, several ion fragments can be produced from molecular targets. A multi-hit time-to-digital-converter was used to allow TOF detection of two or more ion fragments from molecules. This provided partial information on correlations between molecular-fragment ions. The data were recorded in event mode to allow replaying of data to select various coincidence conditions.

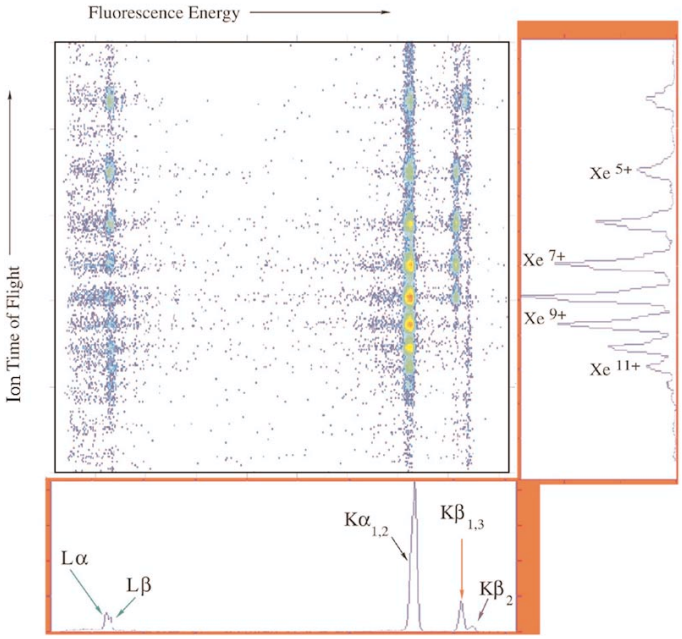

FIG. 1. Xe ions recorded in coincidence with x-ray fluorescence following photoabsorption 30 eV above the K edge.

Results and Discussion

Figure 1 shows a two-dimensional scatter plot of Xe ions recorded in coincidence with x-ray fluorescence following photoabsorption at 30 eV above the K edge. Projections onto the ion-TOF and fluorescence-energy axes show that both the charge states and fluorescence lines are fairly well resolved. The data will be analyzed in various ways, for example, by comparing the different ion charge-state distributions that are correlated with Kα and Kβ fluorescence transitions that are the first steps in the

vacancy cascades. Such data were recorded at several incident energies across the K edge to study how the ion charge state distribution is affected by resonance and threshold excitation.[3] Similar data sets were recorded for Kr excited across its K edge and for $CBrF_3$ excited across the Br K edge.

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