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Synchrotron Radiation Inner-Shell Photoionization
of Atomic and Molecular Gases

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Abstract

A time-of-flight (TOF) spectrometer has been used to measure the average kinetic energies of near thermal atomic and molecular ions, as well as energetic molecular ion fragments, produced by inner-shell photoionization of atomic and molecular gas targets using x rays from the National Synchrotron Light Source (NSLS). While atomic and molecular ions acquire very little energy from the initial photoionization event and subsequent vacancy cascades, multiply charged molecular ions decompose rapidly, producing fragment ions which have kinetic energies determined by their configuration at the moment of decomposition. The strong effects observed suggest that this technique may be extended to the study of configurations of free molecules as well as the orientation of molecules adsorbed on surfaces.

1. Introduction

Highly-charged ions are produced at near thermal energies by x-ray photoionization of inner-shell electrons in atomic gas targets [1]. Subsequent vacancy cascades lead to a distribution of highly-charged ions that acquire only very little initial energy as a result of photoelectron and Auger-electron ejection. However,

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inner-shell vacancies in atomic constituents of molecular gas targets lead to Auger cascades often resulting in unstable highly-charged molecular ions which decompose rapidly into energetic ionic fragments. The kinetic energies of these molecular fragments are determined by the configuration of the molecular constituents just prior to the molecular decomposition and "coulombic explosion" [2]. By investigating the energies of such molecular fragments, information concerning the structure of the parent molecule may be gained.

2. Experimental Procedure

Our TOF analyzer [1], an improved version of traditional TOF analyzers [3], has been modified to allow detection of electrons ejected during the ionization event to be used as a timing reference. Figure 1 shows the standard timing scheme used. The TOF analyzer has a total length of approximately 9 cm and consists of a gas cell with an extraction field, a subsequent acceleration field, a short field free drift region, another acceleration field, and a final long drift region. The addition of the short drift region and the third field region allows us to compensate for the finite width of the ion source, but with a shorter total spectrometer dimension than that used by Wiley and McLaren [3]. Our timing resolution is sufficient to resolve not only high charge states of heavy ions (e.g. Xe +12 and Xe +13), but adjacent mass isotopes as well.

White x rays, attenuated below 3 keV by Be windows, from the NSLS storage ring were used to photoionize gas targets at a typical gas cell pressure of 0.5 mtorr. Energetic electrons (>100 eV) were used as a

start signal to a LeCroy 4201 TDC which was stopped upon the arrival of an ion. Electrons and ions were detected by MCP detectors; signals were amplified and filtered by standard NIM timing electronics.

3. Results and Discussion

To extract kinetic energies from our TOF data, charge-state spectra were taken at different sets of scaled analyzer electric field values (E). The total flight time of the ions is proportional to $\sqrt{m/qE}$, while the width of the TOF peaks is determined by three separate contributions which add in quadrature: a constant electronic timing contribution, independent of field value; a contribution arising from field fringing and imperfect compensation for finite source width (only first order "time focusing" is expected) which scales as $\sqrt{1/qE}$; and a third contribution resulting from the vector velocity distribution of the ions at creation. Ions originally headed away from the detector must be turned around and consequently arrive after those originally headed towards the detector. This difference in time is

$$(\Delta T)_{RE} = \frac{2\sqrt{2mU_0}}{qE}$$

indicating that the initial energy (U_0) of the ions produces a contribution which scales as $1/qE$ [3]. Hence, kinetic energies can be extracted by fitting FWHM of the TOF peaks to the functional form

$$(\Delta T)^2 = a + b/(qE) + c/(qE)^2 .$$

Typical TOF spectra are shown in Figure 2 for an atomic target and a molecular target. For near thermal ions, such as Ar $+q$, the peaks are very narrow indicating very low energy ions. The spectrum in Fig. 2b is that of a linear triatomic molecule, CO₂. The peak of the near thermal molecular ion CO₂ $+2$ is very narrow, while the peaks from the fragment ions are much broader. A closer inspection of the relative widths of the fragment ion peaks reveals the linear nature of the molecule, with carbon being the central atom. The C $+q$ ions appear to be much colder than the O $+q$ ions, due to the mutual cancellation of repulsion from the two O $+q$ ions. The O $+q$ ions, however, leave with high kinetic energy due to coulomb repulsion. Another indication of high kinetic energies for the O $+q$ ions are the dips in the corresponding peaks. They appear whenever ions have sufficient transverse (relative to TOF spectrometer axis) velocity to drift out of the field of view of the spectrometer. Measurements of kinetic energies, with significantly lower error bars than those previously published [4], should be possible by exploiting the sub-nanosecond nature of the excitation, the high intensity of x-rays available from electron storage rings, and the excellent timing properties of our TOF spectrometer.

By using monochromatic photons and selecting specific sites for ionization (e.g., the K shell of a heavy constituent atom in a molecule otherwise composed of light atoms) one may investigate the effects of site specific damage of complex molecular targets. In addition to kinetic energy measurements, angular distribution measurements of molecular fragmentation may be used to investigate configurations of

free molecules and possibly the orientation of molecules adsorbed on surfaces [5].

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Figure Captions

Figure 1. TOF spectrometer and timing schematic. Typical gas cell target pressure was 0.5 mtorr.

Figure 2. (a) Charge state distribution of Ar following K-shell vacancy production. (b) Fragment ion distribution of CO₂ following coulombic explosion resulting from K-shell vacancy production in constituent atom. Time scales are not the same for (a) and (b).