High resolution pulsed field ionization photoelectron spectroscopy using multi-bunch synchrotron radiation: time-of-flight selection scheme

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INTRODUCTION

We have developed an efficient electron time-of-flight (TOF) selection scheme for high resolution pulsed field ionization (PFI) photoelectron (PFI-PE) measurements using monochromatized multi-bunch undulator synchrotron radiation at the Advanced Light Source. By employing a simple electron time-of-flight (TOF) spectrometer, we show that PFI-PEs produced by the PFI in the dark gap of a synchrotron ring period can be cleanly separated from prompt background photoelectrons. The rotational-resolved PFI-PE band for H_2^+ ($X^2\Sigma_g^+$, $v^+=0$) measured using this electron TOF selection scheme is nearly free from residues of nearby autoionizating features, which were observed in the previous measurement by employing an electron spectrometer equipped with a hemispherical energy analyzer. In addition to attaining a high PFI-PE transmission, a major advantage of the electron TOF scheme is that it allows the use of a smaller pulsed electric field and thus results in a higher instrumental PFI-PE resolution. We have demonstrated instrumental resolutions of 1.0 cm^{-1} (FWHM) and 1.9 cm^{-1} (FWHM) in the PFI-PE bands for $Xe^+(^2P_{3/2})$ and $Ar^+(^2P_{3/2})$ at 12.123 eV and 15.760 eV, respectively.

EXPERIMENT

The electron TOF spectrometer used in this study has been modified from the one used in our previous experiments. The main difference was that the hemispherical analyzer has been removed. A schematic diagram showing the present lens arrangement for the electron and ion TOF detection can be seen in Fig. 1. The distance between lenses I1 and E1 was 1.0 cm. The mid-point between lenses I1 and E1 defined the PI/PEX region. The apertures in lenses E1 and E4 used here were 10 mm and 2 mm in diameter, respectively. Micro-spherical plates (MSP) were used for the electron detection.

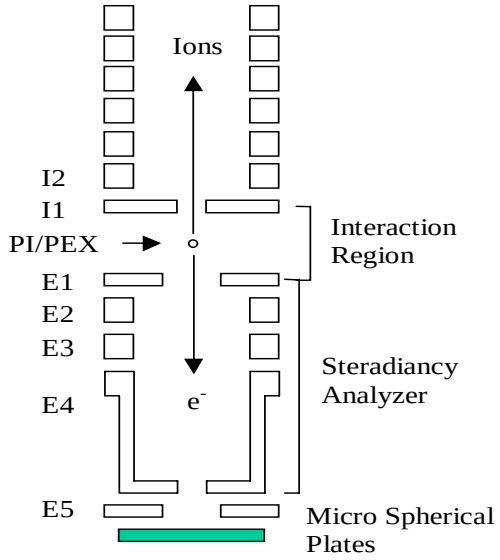

Figure 1 Schematic diagram showing the electrostatic lens arrangement, the ion and electron TOF spectrometer. The electron and ion detectors are micro-spherical plates (MSP).

Figure 2(a) shows the emitting pattern of the ALS light pulses in multi-bunch mode. Following a delay of some 20-60 ns with respect to the beginning of the 112-ns dark gap, an electric field pulse in the range of 0.3-1.5 V/cm was applied to lens E1 [see Fig. 2(b)]. The frequency of the electric field pulse for the PFI was 1.53 MHz, consistent with the ring period.

When the photon energy was set to coincide with the $Ar^+(^2P_{3/2})$ PFI-PE peak at 15.7596 eV, the observed TOF spectrum (solid circles) for PFI-PEs was found to exhibit a single peak with a full width of ≈40 ns as shown in Fig. 2(c). We note that the time zero of the TOF spectra shown in Fig. 2(c) corresponds to the triggering bunch-marking pulse provided by the ALS, the position of which is arbitrary. As the photon energy was slightly increased above the IE for the formation of $Ar^+(^2P_{3/2})$, the single TOF peak for PFI-PEs disappears and an electron TOF spectrum for prompt electrons resembling the synchrotron orbit pattern was observed as these electrons are extracted continuously by the small dc field. The electron TOF spectrum (open circles) observed using a 1.5 V/cm Stark pulse with the photon energy set at 15.7655 eV corresponding to the position of the Ar(11s') autoionizing Rydberg state is also shown in Fig. 2(c). In this spectrum, a small electron signal due to prompt electrons was observed uniformly in time except in a window of ≈110 ns corresponding to the width of the dark gap, where essentially no electrons were formed.

The location of the TOF peak for PFI-PEs in the TOF spectrum depends on the

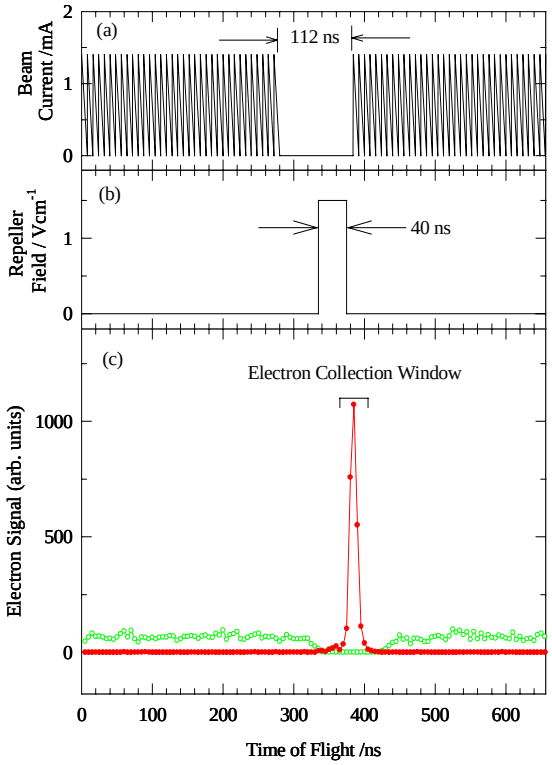

Figure 2 The timing structures for (a) the pattern of VUV light bunches emitted in the ALS multi-bunch mode; (b) the electric field pulses applied to lens E1 (see Fig. 1); and (c) the electron TOF spectra of PFI-PEs (●) as observed at the $Ar^+(^2P_{3/2})$ PFI-PE peak and hot or prompt electrons (○) as observed at the Ar(11s') autoionizing state.

height of the Stark pulse and the delay with respect to the beginning of the dark gap. These parameters were adjusted such that the TOF peak for the PFI-PEs fell in the middle of the 110-ns TOF window where no hot electrons were observed and thus achieved a clear separation of prompt electrons from PFI-PEs. As a result, PFI-PEs can be easily detected free from background prompt electrons by setting a gate with a width corresponding to the width of the TOF peak for PFI-PEs as shown in Fig. 2(c).

RESULTS

In order to illustrate the superior performance of the TOF PFI-PE scheme as compared to the previous synchrotron based PFI-PE method in terms of the achievable resolution and prompt electron background suppression, we show below the PFI-PE spectra for $Xe^+(^2P_{3/2})$, and $H_2^+(v^+=0, N^+)$ obtained using the TOF PFI-PE method.

A. PFI-PE bands for Xe^+ ($^2P_{3/2}$)

As pointed out before, the previous PFI-PE detection scheme using a hemispherical energy analyzer requires a sufficiently high Stark pulse for attaining a high electron transmission. The relatively high Stark pulse required also limits the attainable PFI-PE resolution. The transmission of PFI-PEs in this TOF selection scheme does not have a strong dependence on the applied pulsed electric field. Figures 4(a) shows the PFI-PE bands of $Xe^+(^2P_{3/2})$ in the regions of 12.128-12.131eV, measured using the TOF PFI-PE detection method. The pulsed field used in these measurements was ≈0.3 V/cm. The Gaussian fit to these PFI-PE spectra reveals a resolution of 1.0 cm^{-1} (FWHM) for the $Xe^+(^2P_{3/2})$ bands. This resolution is more than a factor of two better than the best resolutions recorded for these PFI-PE bands in previous ALS experiments and is close to the best resolution (0.8 cm^{-1}, FWHM) reported using VUV laser PFI-PE techniques at ≈18 eV.

B. PFI-PE band for H_2^+ ($X\ ^2\Sigma_g^+$, $v^+ = 0$)

The PFI-PE spectrum for H_2^+ ($X\ ^2\Sigma_g^+$, $v^+ = 0$) in the energy range of 15.34-15.47 eV obtained using the TOF PFI-PE scheme with a 0 V/cm dc field at the PI/PEX region and 1.5 V/cm Stark pulsed field is depicted in Fig. 4(a). Using the 2400 lines/mm grating and monochromator entrance/exit slits sizes

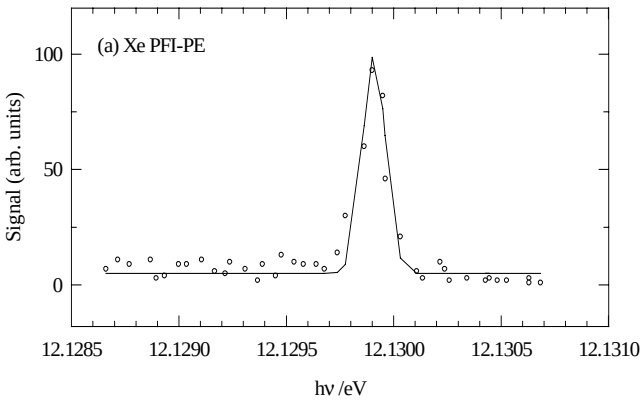

Figure 3 (a) PFI-PE band for $Xe^+(^2P_{3/2})$ (open circles) obtained using a pulsed field of 0.3 V/cm. A Gaussian fit obtained using a least squares fit is also shown (line), revealing a FWHM maximum of 1.0 ± 0.2 cm^{-1}.

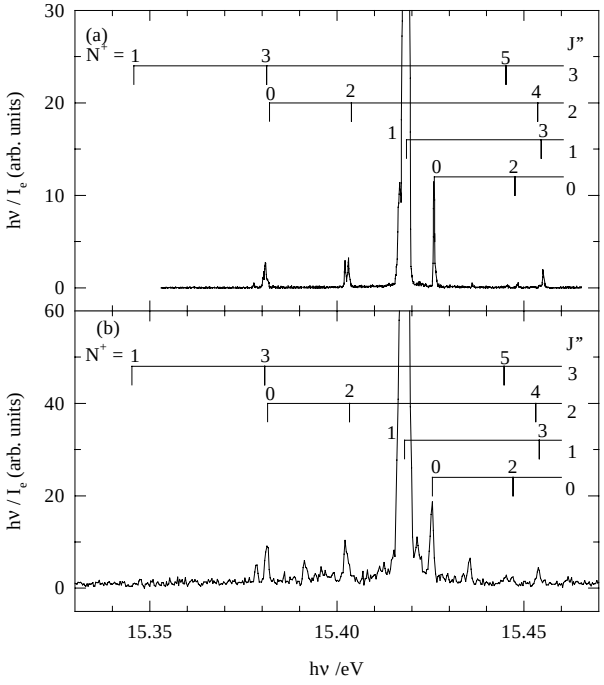

Figure 4 PFI-PE spectrum for H_2^+ ($X^2\Sigma_g^+$, $v^+ = 0$) recorded (a) using electron TOF analysis with a 0 V/cm dc field , and a 1.5 V/cm pulsed field across the interaction region. The 4800 lines grating was used. The monochromator entrance/exit slits are set at 10/10 μm corresponding to a nominal resolution of 0.0064 Å (FWHM), (b) using a hemispherical and steradiancy analyzer in tandem and a 0.67 V cm^{-1} pulsed field at a nominal wavelength resolution of 0.048 Å (FWHM).

of 10/10 μm, the nominal wavelength resolution used was 0.0064 Å (FWHM). Figure 4(b) shows the H_2^+ ($X\ ^2\Sigma_g^+$, $v^+ = 0$) spectrum in the same energy range recorded previously using a tandem steradiancy-hemispherical spectrometer at a nominal optical resolution of 0.048 Å [see Fig. 4(b)].

In the previous experiment, we had examined the achievable resolution by using a higher wavelength resolution and found that the observed PFI-PE resolution could not be significantly improved because of contamination by strong nearby autoionizing resonances as shown in Fig. 4(b). In view of this pervious exercise, we may conclude that the higher resolution observed in Fig. 4(a) is due partly to a better suppression of prompt electrons.

Since the spectrum of Fig. 4(a) is essentially free from contamination of autoionizing resonances, it provides a more reliable measure for the relative photoionization cross sections of the marked rotational transitions. Based on the FWHM of the (0, 0) transition, we estimate that the PFI-PE resolution for the spectrum of Fig. 4(a) is 2.5 cm^{-1} (FWHM), significantly higher than ≈7 cm^{-1} (FWHM) attained in the spectrum of Fig. 4(b).

SUMMARY

The spectra presented in Figs. 4(a) and 4(b) have demonstrated that the TOF PFI-PE detection method described here is superior compared to the previous synchrotron based PFI-PE measurement schemes in both resolution and background electron suppression. The basic difference between this and the previous arrangement is that the hemispherical energy analyzer is eliminated in the present setup. Consequently, the electron transmission through the analyzer should be higher. Since the TOF axis is perpendicular to the VUV light beam, the TOF resolution is determined only by the height of the VUV beam along the TOF axis. It should be possible to significantly increase the PFI-PE signal by enlarging the entrance and exit apertures of the TOF spectrometer without affecting the TOF resolution.

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