Pulsed Field Ionization-Photoion Spectroscopy Using Two-Bunch Synchrotron radiation: Time-of-Flight Selection Scheme

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INTRODUCTION

We have demonstrated that the time-of-flight selection method for pulsed field ionization (PFI) photoelectron detection [Jarvis et al., Rev. Sci. Instrum. **70**, 2615 (1999)] can also be applied for the detection of PFI-photoions (PFI-PIs) using the two-bunch synchrotron radiation at the Advanced Light Source. By employing the supersonic beam technique to lower the translational temperature of the sample gas, we show that background prompt ions formed in direct and spontaneous autoionization processes arrive at the ion detector in a pattern similar to that of the VUV light bunches. The PFI-PIs formed at dark gaps can be designed to arrive at the detector in between adjacent prompt ion peaks, enabling the gating of the PFI-PI signal with only minor contamination from background prompt ions. This experiment has revealed important considerations for the design of a general TOF selection scheme for PFI-PI detection using synchrotron radiation.

EXPERIMENTAL CONSIDERATIONS

The detailed photoelectron-photoion apparatus have been described in details previously. The ALS storage ring is capable of filling 328 electron buckets in a period of 656 ns in multi-bunch mode. In the two-bunch mode, there are only two 50 ps bunches of electrons separated by 328 ns making up the synchrotron ring period. Thus, we may view the dark gap (light-off period) in the two-bunch operation as 326 ns. All experiments described here were carried out while the synchrotron was operating in the two-bunch mode, where each electron bunch was filled to 25 mA. Ion TOF spectra were recorded using a multichannel scaler triggered by the bunch marker, a pulse sent out by the ALS for every ALS period (656 ns) or two VUV light bunches in the two-bunch mode. Timing gates were applied using a 622 LeCroy coincidence unit to gate the ion signals of interest.

The idea of the present experimental scheme for the detection of PFI-PIs derives from our recent development of PFI-PE measurements using the TOF selection method to separate prompt electrons from PFI-PEs. However, the separation of PFI-PIs from background prompt ions using the TOF selection scheme would require a significantly larger dark gap. For this reason, the PFI-PE measurements described here were all performed using two-bunch synchrotron radiation, where the dark gap is 326 ns.

The ions are extracted not only by the constant dc field of 1.74 V/cm, but also the 3.05 MHz PFI field. One of the purposes of using of a relatively high PFI field of 8.7 V/cm here is to aid extraction of PFI-PIs. The H_2^+ and Ar^+ ions are expected to spend more than 1 μs in the PI/PEX region, corresponding to several pulsing cycles. That is, these ions in the present experiment see a quasi-continuous acceleration field, which is estimated to be equivalent to an effective F value of ≈ 3-4 V/cm.

RESULTS

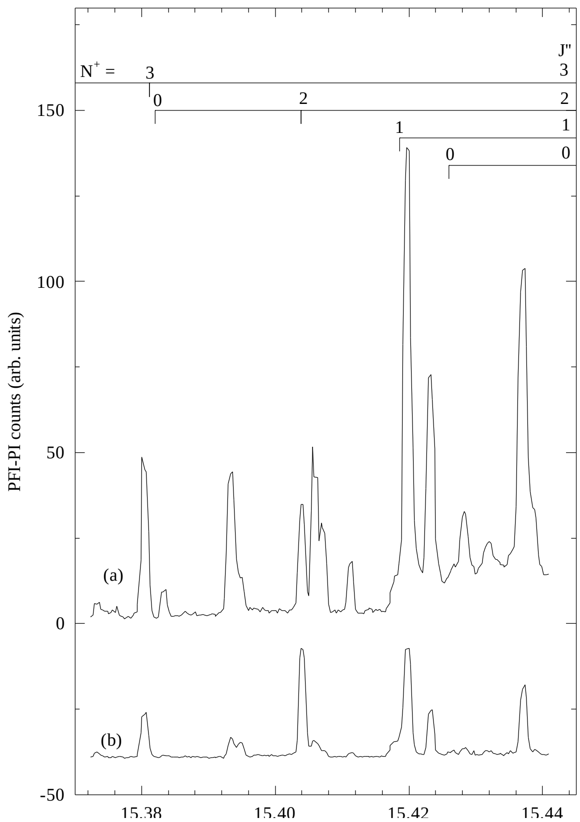

Figure 1. (a) PIE spectrum and (b) PFI-PI spectrum for H_2 in the photon energy range of 15.37-15.44 eV obtained by measuring the prompt ion and PFI-PI peak intensities, respectively, using an 80-ns time gate. The positions of rotational transitions (N^+, J″) are marked at the top of the figure. The peaks observed at 15.395, 15.423, and 15.437 eV in the PFI-PI spectrum are attributed to residues of autoionization resonances.

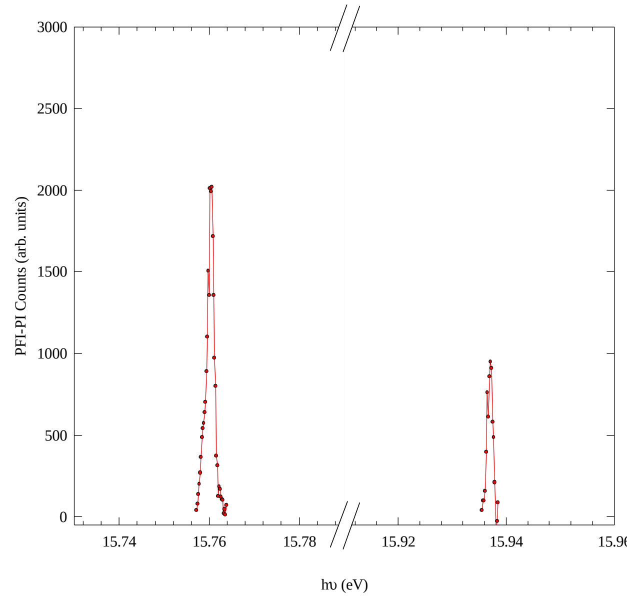

Figure 2. PFI-PI bands for (a) $Ar^+(^2P_{3/2})$ and (b) $Ar^+(^2P_{1/2})$ obtained by measuring the PFI-PI intensity using a 100-ns time gate, together with background corrections described in the text. Note that the ratio for the relative intensities for the $Ar^+(^2P_{3/2})$ and (b) $Ar^+(^2P_{1/2})$ PFI-PI bands is about 2:1.

A. PFI-PI band for $H_2^+(v^+ = 0, N^+$¬ J²)

By measuring the intensities for the prompt ion and PFI-PI peaks as a function of photon energy using an 80 ns time gate, we have obtained the spectra in the energy region of 15.37-15.44 eV shown in Figs. 1(a) and 1(b), respectively. The positions of ionization rotational transitions (N^+, J″) are marked on the top of Fig. 1. As expected, the spectrum of Fig. 1(a) is identical to the photoionization efficiency (PIE) spectrum for H_2^+, which is known to be dominated by strong autoionization structures. We note that the main peaks observed in the spectrum of Fig. 1(b) can be assigned to rotational transitions (1, 1), (2, 2), and (3, 3), supporting the conclusion that this spectrum is mostly the PFI-PI band for $H_2^+(v^+ = 0, N^+ \leftarrow J'')$. Due to the very strong autoionizing Rydberg states for H_2 in this energy region, residues from many prominent Rydberg resonances, especially those at 15.395, 15.423, and 15.437 eV, are discernible in the PFI-PE band for $H_2^+(v^+=0, N^+ \leftarrow J'')$ obtained previously using an electron spectrometer. Thus, it is not surprising that Rydberg residues at 15.395, 15.423, and 15.437 eV are also observed in the PFI-PI spectrum of Fig. 1(b).

B. PFI-PI spectra for Ar^+ ($^2P_{3/2}$) and Ar^+($^2P_{1/2}$)

Although the complete separation of the TOF peaks for Ar^+ PFI-PIs and prompt ions is not possible with the dark of 326 ns, the simulation indicates that the contribution of background prompt ion signal at the PFI-PI peak can be reliably estimated. By employing a time gate of 100 ns centered at the Ar^+ PFI-PI ion peak, together with the correction of prompt ion background, we obtain the PFI-PI bands for Ar^+($^2P_{3/2}$) and Ar^+($^2P_{1/2}$) as shown in Fig. 2. The FWHMs of these bands show that the PFI-PI resolution achieved is about 1 meV (FWHM). The observed intensity ratio for the Ar^+($^2P_{3/2}$) and Ar^+($^2P_{1/2}$) PFI-PI bands is about 2:1, demonstrating that the detection of PFI-PIs resulting from the PFI of short-lived high-n Rydberg states, which converge to the excited Ar^+($^2P_{1/2}$) threshold, is highly effiecient. Thus, we may conclude that the PFI-PI detection scheme described here is far superior to that used in our previous MATI study, where the PFI-PI band for Ar^+($^2P_{1/2}$) was not observed.

DISCUSSION

This experiment shows that a dark gap of 326 ns is adequate for separating the PFI-PIs and prompt ions for H_2^+. The thermal H_2 sample is found to be responsible for the minor prompt ion background observed in the detection of H_2^+ PFI-PIs. We expected that this prompt ion background arising from photoionization of thermal background H_2 in the PI/PEX region can be significantly reduced by the use of a low temperature ion source. To achieve this, a good insulation of the PI/PEX region from the photoionization chamber is required, such that background H_2 at the PI/PEX region can maintain the same temperature of the wall of the ion source. By employing a commercial He-compressor, it is possible to design a low temperature H_2 sample cell cooled to ≈20 K. Using such a low temperature H_2 cell, the PFI-PI and prompt ion peaks should be completely resolved with a dark gap of 326 ns. Furthermore, when such a low temperature cell is used, the employment of the supersonic beam technique to introduce the H_2 sample into the PI/PEX region becomes unnecessary.

For the PFI-PI measurement of Ar^+ and other ions with a higher mass than H_2^+, the success would require the use of a larger dark gap. This can be achieved by mechanical chopping the synchrotron VUV beam. If we use the same ion extraction and PFI conditions as described in the present experiment, the clean separation of the PFI-PI and prompt Ar^+ ion peaks would require an on/off VUV pattern of ≈1.0/1.0 μs. Since the dark gap required for PFI-PI measurements depends on the mass of the ion of interest, the use of a chopper wheel to chop the ALS beam is a sound approach because the dark gap can be adjusted to suit the experimental requirement.

REFERENCE

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