ADVANCES IN PHOTOELECTRON SPECTROSCOPY USING THIRD GENERATION UNDULATOR SYNCHROTRON RADIATION

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We have demonstrated a novel experimental scheme for pulsed field ionization photoelectron (PFI-PE) measurements using the monochromatized multi-bunch undulator synchrotron source at the Chemical Dynamics Beamline of the Advanced Light Source (ALS). [1] In this technique, high-n (n$\geq$100) Rydberg states are field ionized by a small electric field applied in the dark gap of a synchrotron ring period. Using an electron spectrometer equipped with a steradiancy analyzer and a hemispherical electron energy analyzer, we have shown that PFI-PEs can be detected with little prompt electron background for a delay of only 8 ns with respect to the beginning of the dark gap. This scheme overcomes the requirement for a delay in the μs range in laser PFI-PE studies. The greatest advantage of synchrotron radiation is the ease of tunability in the full vacuum ultraviolet (VUV) range of 6-30 eV, meaning that vibronic photoelectron progressions arising from valence shell ionization of all molecular species can be studied in their entirety with rotational resolution. Recently, we have further developed an efficient electron time-of-flight (TOF) selection scheme for PFI-PE studies. [2] By employing a simple TOF spectrometer, we show that PFI-PEs produced by the PFI in the dark gap can be cleanly separated from prompt electrons. A near complete suppression of prompt electrons was achieved by gating the PFI-PE TOF peak. We have demonstrated instrumental resolution of 1.0 cm^{-1} (FWHM), which is close to the best [0.8 cm^{-1}(FWHM)] achieved in VUV laser PFI-PE experiments. Using these new experimental methods, we have obtained rotationally resolved vibrational progressions for many diatomic and triatomic molecules close to their dissociation limits. [1] The analyses of PFI-PE bands for highly vibrationally excited diatomic ions, [3] O_2^+, NO^+, and CO^+ will be presented.

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[a] C. Y. Ng, in "Photoionization and Photodetachment", edited by C. Y. Ng (World Scientific, Singapore, 1999),*Adv. Ser Phys. Chem.*, Vol.10A, in press.

[b] G. K. Jarvis, Y. Song, and C. Y. Ng,*Rev. Sci. Instrum.*, submitted.

[c] G. K. Jarvis, Y. Song, and C. Y. Ng, *J. Chem. Phys.*, submitted.