DELAYED IONIZATION OF UO₂ AND PFI-ZEKE SPECTRA FOR UO₂⁺

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The decay dynamics of threshold ionization of UO₂ have been examined using a 1+1 REMPI technique. Ionization is accomplished via resonant excitation of the 2g ← X 3Φ2u transition of UO₂ at 314.09 nm, followed by ionization just above threshold using a second tunable dye laser operating at λ ≤ 573 nm. While the peak widths for U⁺ and UO⁺ in the time of flight mass-spectrum are limited by the experimental resolution, the peak for UO₂⁺ is significantly broader, showing a characteristic decay towards longer flight times, which is the result of delayed ionization. The lifetime of this process is approximately 100 nanoseconds (at threshold) and decreases exponentially as the ionizing laser is tuned higher in energy.

The ionization potential (IP) of UO₂ has been measured previously, namely 6.128(3) eV, using photoionization efficiency curves. Refinement of the IP using mass analyzed threshold ionization (MATI) spectra was unsuccessful, as the delayed ionization may have interfered with this detection technique [J. Han et al. J. Chem. Phys. 120, 5155 (2004)]. Here we report high-resolution pulsed-field ionization zero kinetic energy photoelectron (PFI-ZEKE) spectra which have allowed a more accurate determination of the IP of UO₂, as well as providing a spectroscopic probe of UO₂⁺. Accurate values for the electronic term energies and vibrational frequencies of UO₂⁺ have been obtained. A comparison of the current experimental results with theoretical calculations will be presented.