DELAYED IONIZATION OF UO_2 AND PFI-ZEKE SPECTRA FOR UO_2^+

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The decay dynamics of threshold ionization of UO_2 have been examined using a 1+1 REMPI technique. Ionization is accomplished via resonant excitation of the 2g $\leftarrow$ X $^3\Phi 2u$ transition of UO_2 at 314.09 nm, followed by ionization just above threshold using a second tunable dye laser operating at $\lambda \leq 573$ 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 UO_2^+ 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 UO_2 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 UO_2, as well as providing a spectroscopic probe of UO_2^+. Accurate values for the electronic term energies and vibrational frequencies of UO_2^+ have been obtained. A comparison of the current experimental results with theoretical calculations will be presented.