IONIZATION ENERGY MEASUREMENTS AND SPECTROSCOPY OF HfO AND HfO^+

J. M. MERRITT, V. E. BONDYBEY, and M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322*.

Rotationally resolved spectra of the HfO^+ cation have been recorded using the pulsed field ionization zero electron kinetic energy (PFI-ZEKE) technique. The $F(0^+) \leftarrow X^1\Sigma_g$ band system in HfO was resonantly excited to provide vibrational and rotational state selectivity in the two photon ionization process. Using the PFI-ZEKE technique a value of 7.91687(10) eV was determined for the ionization energy (IE) of HfO, 0.37 eV higher than the values reported previously using electron impact ionization measurements. Underestimation of the IE in the previous studies is attributed to ionization of thermally excited states. A progression in the HfO^+ stretching vibration up to $\nu^+ = 4$ was observed in the PFI-ZEKE spectrum, allowing for determination of the ground electronic state vibrational frequency of ν_e = 1017.7(10) cm^{-1} and anharmonicity of $\omega_e x_e$ = 3.2(2) cm^{-1}. The rotational constant of HfO^+ was determined to be 0.403(5) cm^{-1}. Benchmark theoretical *ab initio* calculations were carried out in order to explore the effects of electron correlation on the predicted molecular properties. Survey scans utilizing laser induced fluorescence and resonance enhanced multiphoton ionization detection revealed many previously unassigned bands in the region of the F-X and G-X bands of HfO, which we attribute to nominally forbidden singlet triplet transitions of HfO.