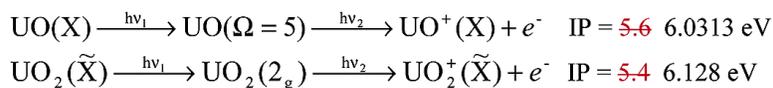


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Accurate Ionization Potentials for UO and UO₂: A Rigorous Test of Relativistic Quantum Chemistry Calculations

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Experimental studies of radioactive actinide compounds are expensive and hazardous. Consequently, efforts are underway to develop computational methods that are capable of making reliable predictions of the properties of actinide compounds in general. This is a challenging problem that is compounded by the lack of data suitable for providing rigorous tests of the theoretical predictions. Calculations are typically performed for isolated molecules, but there have been few studies of actinide compounds in the gas phase.

As most of the gas-phase studies conducted to date have relied on mass spectrometry techniques, the ionization potentials (IPs) have been measured for a number of actinide oxides and halides.¹ For the simplest oxides of uranium, UO and UO₂, the currently accepted values for the IPs are 5.6 ± 0.1 and 5.4 ± 0.1 eV, respectively.^{2–4} Large-scale electronic structure calculations for UO₂ consistently predict a much higher value for the IP, in the range of 6.0–6.3 eV.^{5–7} Gagliardi et al.⁶ considered their calculations to be of sufficient reliability to question the validity of the experimental results. While there have been fewer attempts to calculate the IP of UO, the published predictions (6.17⁸ and 5.71⁹ eV) also exceed the accepted values. The primary weakness of the experimental studies is that high-temperature sources are used to provide gas-phase oxides. Molecules trapped in metastable electronically excited states are present in these vapors, possibly resulting in the underestimation of IPs derived from appearance potentials or photoelectron spectra.

Beyond the issue of testing theoretical methods, the true IPs of UO and UO₂ are a matter of practical significance, as these data are used in calculating other thermodynamic properties.¹ In the present work, we have re-examined the IPs using resonantly enhanced multiphoton ionization (REMPI) and mass-analyzed threshold ionization (MATI)¹⁰ techniques. These methods permit selective ionization of molecules from the ground state.

Gas-phase samples of U, UO, and UO₂ were generated by pulsed laser vaporization of a uranium target. The ablated plume was entrained in a flow of He that contained 0.1% O₂ to facilitate oxide formation. The resulting gas mixture was cooled by supersonic expansion, and the core of the expanding gas was transmitted to a time-of-flight mass spectrometer. The metal oxides were photoionized in the source region of the spectrometer by 10-ns laser pulses from two tunable dye lasers (both operated with line widths of 0.3 cm⁻¹). Two-photon sequential ionization via resonant intermediate states was used to record excitation spectra and determine ionization thresholds. MATI experiments were performed with a spoiling field of 15 V cm⁻¹. The depression of the IP caused by this field was taken into account. The calibration of the instrument was evaluated by measuring the IP of atomic U. A value of 49 959(1) cm⁻¹ was obtained, in excellent agreement with the most recent determination (49 958.4(5) cm⁻¹).¹¹

A careful search was made to locate the IP of UO within the expected range (5.3–5.5 eV), with the first laser tuned to the Q-branch feature of the [17.613]5-X1(4) transition^{12,13} at 17 613.97

cm⁻¹. However, the first ionization threshold was not found until the ionizing laser was tuned to the spectral region corresponding to a total excitation energy near 6 eV. An accurate IP for UO was then measured by MATI using two different intermediate excited states. An IP of 48 645(5) cm⁻¹ (6.0313(6) eV) was obtained with the first laser tuned to the [17.613]5-X1(4) transition. As a consistency check, the IP was then measured with the first laser tuned to the Q-branch feature of the [17.653]5-X1(4) transition^{12,13} at 17 653.7 cm⁻¹. A value of 48 647(5) cm⁻¹ was obtained. Despite the use of supersonic cooling, single-photon ionization measurements carried out in our apparatus showed that UO trapped in metastable electronically excited states was present in the beam. It is likely that thermally populated excited states were responsible for the low IPs obtained in the previous investigations.

Electronic spectra for gas-phase UO₂ had not been reported previously. We began our investigation of this molecule by searching for band systems in selected regions of the visible and near-UV spectral ranges. This search was guided by the ab initio calculations of Chang and Pitzer.¹⁴ The ground state of UO₂ is X³Φ_{2u}, derived from the (5f7s) configuration. Chang and Pitzer¹⁴ predicted strong transitions from this ground state that fall in the 540–300 nm range. Many band systems were observed within this range. Mass-selected REMPI spectra recorded in the vicinity of 316 nm revealed the well-resolved group of four bands shown in Figure 1. Similar structures were observed near 572 and 552 nm. The analysis of the visible spectrum will be presented elsewhere. Band I was used in the initial search for the ionization threshold. As with UO, the threshold was found at an energy that was much higher than expected on the basis of previous reports. With the first laser tuned to the maximum of band I at 31 856 cm⁻¹, the IP was located at 49 424(20) cm⁻¹ (6.128(3) eV). The ionization dynamics of UO₂ were found to be more complex than those of UO, and we were unable to obtain MATI spectra. Delayed ionization was observed, with the UO₂⁺ signal decaying with a lifetime of approximately 90 ns. The lifetime was dependent on the excess energy imparted by the second photon and the electric field in the ion source. As the bond dissociation energy of UO₂ (7.85 eV) exceeds the IP, it is probable that field-induced mixing of the high Rydberg states with highly excited valence states is responsible for this effect. The delayed ionization was used to advantage as the threshold observed by detecting the delayed ions was sharper than that observed by detecting the total UO₂⁺ signal. Even so, as the UO₂ IP was derived from the photoionization efficiency curve, the error limits are greater than those achieved in the measurements for U and UO.

Threshold measurements made using bands II, III, and IV (Figure 1) to populate the intermediate state yielded IPs of 49 303, 49 056, and 48 926 cm⁻¹, respectively. When combined with energies for the first photon resonances, these data show that bands I and III terminate on the same upper level. On the basis of the calculations of Chang and Pitzer,¹⁴ we tentatively assign this state as (5f7p)³Φ_{2g}.

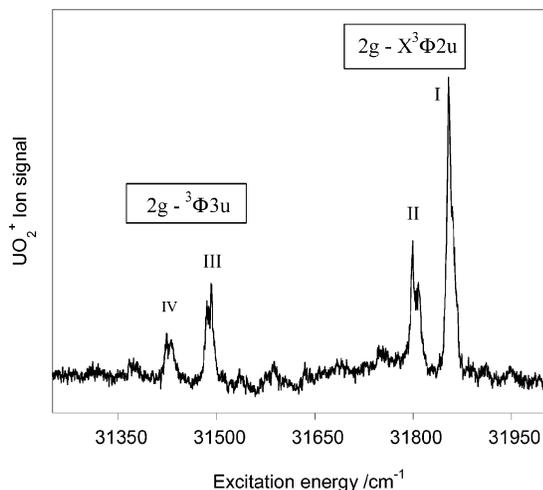


Figure 1. Section of the REMPI spectrum of UO_2 recorded using mass-selected detection of UO_2^+ ions. These are bands of the $(5f7p)2_g \leftarrow (5f7s)-X^3\Phi$ transition.

The lower level of band III, which lies 368 cm^{-1} above the $X^3\Phi_{2u}$ ground state, is assigned to $^3\Phi_{3u}$ (the bands near 572 nm were also found to originate from this level). Previous ab initio calculations predicted $3u-2u$ intervals of 403^6 and 431^{14} cm^{-1} , in reasonable agreement with the present results. Bands II and IV are bending sequence bands ($v_b' = 1 - v_b'' = 1$) originating from the $2u$ and $3u$ states. The lower state bending frequencies derived from these measurements are 121 cm^{-1} ($2u$) and 130 cm^{-1} ($3u$). Ab initio and DFT calculations predicted ground-state bending frequencies in the range of $138-222\text{ cm}^{-1}$.^{5,7} The slightly lower experimental value may indicate that the bending potential is anharmonic (an expected consequence of Renner–Teller vibronic coupling).

Theoretical calculations for UO_2 yielded values for the IP of 6.17 (CASPT2),⁶ 6.19 (B3LYP),⁶ 6.3 (B3LYP),⁷ 6.01 (CCD),⁵ and 6.05 eV (MP2).⁵ Clearly, the present results provide an impressive validation of these predictions. Similarly, the measured IP for UO

is in reasonably good agreement with the value of 6.17 eV obtained by Malli⁸ from an RDF–SCF calculation. In addition to validating the theoretical predictions, the present work highlights the difficulty of obtaining well-defined IPs for prototypical actinide compounds. It is likely that the thermal excitation problems encountered in the study of UO and UO_2 have resulted in the underestimation of the IPs for several other related species.

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