J. Phys. Chem. A 2009, 113, 12353–12355

ARTICLES

On the Ionization Energy of HfO[†]

Hermann Stoll

Institut für Theoretische Chemie, Universität Stuttgart 70550 Stuttgart, Germany

Kirk A. Peterson*

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

Jeremy M. Merritt and Michael C. Heaven

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received: May 27, 2009; Revised Manuscript Received: June 22, 2009

Using a newly developed relativistic pseudopotential and a series of correlation consistent basis sets for Hf, the ionization energy of HfO and the spectroscopic properties of the HfO^+ cation have been determined in coupled cluster calculations. After accounting for basis set incompleteness, outer-core correlation, the pseudopotential approximation, and higher order electron correlation effects, excellent agreement with recent experimental measurements is obtained.

1. Introduction

Accurate ab initio calculation of the ionization energies (IE) of transition metal oxides proves to be a demanding test of basis set quality and correlation methods. In recent years the experimental methods for determining IE have advanced to the point where measurements with relative errors of 10^{-5} are feasible.[1,2] From both spectroscopic determinations[2−6] and systematic studies of charge exchange reactions,[7] it has become apparent that many of the earlier IE measurements for refractory species that utilized electron impact ionization were subject to large systematic errors. As more reliable IE values become available they can be used in the process of evaluating and developing ab initio methods. Pseudopotentials are widely used for the heavier transition metals, and recent studies of ThO, UO, and UO_2 indicated that the calculated IEs are strongly dependent on the size and quality of the pseudopotential core.[8]

The present study of the ionization of HfO is part of an ongoing effort to develop energy-consistent relativistic pseudopotentials and basis sets for the 5d elements. Merritt et al.[3] recently examined HfO using a two-color photoionization technique. They reported an ionization energy of 7.91678(10) eV and spectroscopic constants for the ground state of HfO^+. Their IE value was 0.37 eV higher than that determined previously by electron impact ionization,[9] and 1.1 eV greater than the IE of atomic Hf. The latter indicated a lower bond energy for HfO^+, as compared to HfO. In contrast, the molecular constants indicated a shorter bond length and higher vibrational frequency for the ion. Similar trends had been observed previously for the isoelectronic species ThO.[6]

Merritt et al.[3] also carried out a series of ab initio calculations for comparison with their experimental results. The highest levels of theory they examined were CCSDT and MRCISD(Q). The older Stuttgart ECP60MWB effective core potential and its accompanying basis set[10] was used for Hf. Good agreement between the calculated and measured molecular constants was achieved for both HfO and HfO^+, but the best prediction for the IE was still 0.16 eV below the experimental result. Merritt et al. speculated that this error might be associated with the quality of the basis set for Hf. This issue is further explored here, where the properties of HfO and HfO^+ are calculated using a newly developed relativistic pseudopotential and correlation consistent basis sets for Hf.

2. Calculations and Results

In order to determine the adiabatic ionization energy of HfO, we performed calculations for the potential curve of the HfO^+ molecule, in its $^2\Sigma^+$ ground state using the Molpro program throughout.[17] These calculations closely parallel the corresponding ones for the neutral HfO molecule ($^1\Sigma^+$ ground state),[11] which were performed within a recent benchmark study of newly developed energy-consistent relativistic pseudopotentials (PP) for the 5d elements.[12] The new Hf PP was used together with accompanying series of correlation-consistent polarized valence *n*-zeta (cc-pV*n*Z-PP) and weighted core−valence *n*-zeta (cc-pwCV*n*Z-PP) basis sets with $n = 3-5$.[12] An all-electron description, with augmented correlation-consistent basis sets (aug-cc-pV*n*Z), was used for the O atom.

In a first set of calculations, we determined points of the HfO^+ potential curve at the coupled-cluster level, with single and double excitations from the restricted Hartree−Fock (RHF) reference, perturbatively accounting for triples (CCSD(T)).[18] The Hf and O valence shells were correlated, but no excitations were allowed from the Hf 5sp outer-core orbitals and from the O 1s shell. (Note that the Hf 1s through 4f orbitals are simulated by the PP and can thus be considered as frozen, too.) The cc-pV*n*Z-

---

[†] Part of the "Russell M. Pitzer Festschrift".

* To whom correspondence should be addressed.

10.1021/jp904936x CCC: $40.75

TABLE 1: CCSD(T) Results for the Bond Length r_e (Å) and Harmonic Vibrational Frequency ω_e (cm^{-1}) of HfO$^+$, and the Adiabatic Ionization Energy IE (eV) of HfO[a]

method	basis set	r_e	ω_e	IE
PP, val	cc-pVTZ-PP	1.712	992.9	7.680
	cc-pVQZ-PP	1.709	994.3	7.688
	cc-pV5Z-PP	1.708	995.8	7.690
	CBS	1.708	996.4	7.694
PP, val+cv	cc-pwCVTZ-PP	1.690	1013.5	7.816
	cc-pwCVQZ-PP	1.686	1020.5	7.821
	cc-pwCV5Z-PP	1.684	1023.9	7.823
	CBS	1.683	1027.1	7.826
AE, val	cc-pwCVTZ-DK3	1.726	993.4	7.704
		(+0.019)	(−0.9)	(+0.029)
AE, val+cv	cc-pwCVTZ-DK3	1.710	1009.1	7.839
		(+0.020)	(−4.4)	(+0.023)
AE, val+cv+4f	cc-pwCVTZ-DK3 +4f	1.701	1012.9	7.891
		(−0.010)	(+3.7)	(+0.052)
CCSDT, val	cc-pVTZ-PP	1.711	998.6	7.685
		(−0.002)	(+6.1)	(+0.005)
CCSDTQ, val	cc-pVDZ-PP	1.727	961.8	7.676
		(+0.002)	(−10.0)	(+0.003)
Theory, Best		1.694	1022	7.91
Expt.		1.687(3)	1017.7(10)	7.91687(10)

[a] Pseudopotential (PP) and all-electron descriptions (AE) for Hf, using different sizes of the correlated space (without/with inclusion of the outer-core 5sp shells (val/val+cv) and additional inclusion of 4f shell (+4f)), and different basis set sizes, are compared to experimental results from ref 3. Values in parentheses denote AE-PP differences (val/val+cv), the 4f shell contribution (val+cv+4f), the differences between CCSDT and CCSD(T) and the differences between CCSDTQ and CCSDT. The experimental bond length is a r_0 value.

PP series of basis sets was used and the correlation energy was extrapolated to the basis-set limit for each point of the potential curve, from $n = 4$ and $n = 5$ by means of a $1/n^3$ formula. Points of the potential curve were calculated in steps of 0.03 Å, and seven points around the minimum were fitted by means of a rational interpolation, $\Sigma_{i=-1}^{4} a_i r^i$. Via the usual Dunham analysis,[16] this yields values for the bond length r_e, harmonic stretching frequency ω_e, and, by comparison to the corresponding HfO potential curve, the adiabatic ionization energy IE. Results are listed in Table 1. With a triple-ζ basis set ($n = 3$), r_e comes out too long by 0.025 Å, ω_e is too small by 25 cm^{-1}, and the IE is too low by 0.24 eV, as compared to recent experimental data of Merritt et al.[3] These errors do not become much smaller when improving the basis set to $n = 5$ and extrapolating to $n \to \infty$ (CBS): they are 0.021 Å, −21 cm^{-1}, and −0.22 eV, respectively. Interestingly, the experimentally determined differences between the bond lengths and harmonic wavenumbers of the neutral and ionized molecules HfO and HfO$^+$, respectively, are qualitatively quite well reproduced at this theoretical level: $\Delta r_e = -0.03$ (-0.03) Å, and $\Delta\omega_e = 42$ (45) cm^{-1} at the triple-ζ (CBS) level, in satisfactory agreement with the experimental differential effects of −0.04 Å and 44 cm^{-1}.[13]

In a next step, we refined the theoretical treatment by also correlating the outer-core 5*sp* shell of Hf within the CCSD(T) calculations. The series of cc-pV*n*Z-PP basis sets for Hf was replaced by the more flexible cc-pwCV*n*Z-PP one, and calculations were again performed for $n = 3 - 5$, and the data for $n = 4$ and 5 were used for extrapolating the correlation energy to the CBS limit. At the triple-ζ level, r_e becomes smaller by 0.02 Å, ω_e larger by 21 cm^{-1}, IE by 0.14 eV, i.e., the difference to experiment becomes consistently smaller, cf. Table 1. Also, the basis-set dependence is more pronounced than within the valence-only treatment, especially for ω_e. Thus, the CBS-limit differences to experiment are now just −0.004 Å, 9 cm^{-1}, and 0.09 eV, for r_e, ω_e, and IE. Since the experimental bond length is an effective $v = 0$ value, the agreement with the theoretical result is further improved by utilizing the ab initio value of α_e, the vibration−rotation interaction constant, which is calculated to be 52 MHz at the CCSD(T) CBS limit with the 5sp shell of Hf correlated. The difference between r_0 and r_e is then determined to be +0.0018 Å, and the application of this result nearly halves the difference to the experimental r_0 value. The ab initio value for the vibrational anharmonicity constant $\omega_e x_e$ at this same level of theory, 3.37 cm^{-1}, is also in excellent agreement with the value determined from experiment, 3.2 ± 0.2 cm^{-1}.

In order to quantify errors intrinsic to the pseudopotential treatment considered so far, we performed benchmark all-electron calculations employing a third-order Douglas−Kroll−Hess (DKH)[13,14] approach for including scalar-relativistic effects. We used a specially optimized all-electron triple-ζ (cc-pwCVTZ-DK3) basis set for Hf.[12] Since for HfO the Hf 4f orbitals are higher in energy than the 5sp ones, and there is also a mixing of these orbitals with O 2s, we used Hf 4f and 5sp orbitals taken from the free atom in order to define uncorrelated cores that can be compared to the ECP treatment. The same cores were used for HfO and HfO$^+$. For investigating the influence of correlation effects of the 4f shell, we subsequently reoptimized the 4f orbitals in the molecular surroundings and added f and g functions suitable to describe correlation of this shell to the basis set (cc-pwCVTZ-DK3+4f).[12] When comparing the results of the all-electron calculations to ECP ones with basis sets of comparable (triple-ζ) quality, we find differences that slightly depend on the correlated orbital space (with/without inclusion of 5sp correlation): the bond length of HfO$^+$ increases by ~0.02 Å, the vibrational frequency changes very little (by 1 − 4 cm^{-1}), and the ionization energy becomes larger by 0.02−0.03 eV. The correlation effect of the 4f shell (which is absent in the ECP calculations, where the 4f orbitals are attributed to the core simulated by the ECP) leads to changes of about the same magnitude: a bond-length change of −0.01 Å partly counteracts the AE-PP deviation discussed above, and the same holds true for the change of the stretching frequency. In contrast to that, 4f correlation contributions enhance the IE value by another 0.05 eV. Finally, relaxing the Hf 1s−4d frozen core, within the all-electron calculation including 4f correlation, leaves r_e and IE practically unchanged, but reduces ω_e by 3 cm^{-1}.

The appropriateness of using only a third-order DKH approach in the above calculations was also checked for both HfO and HfO$^+$ at the CCSD(T) level of theory with cc-pwCVTZ-DK+4f basis sets and correlating the valence and 4*f* electrons. Compared to the DKH3 results, the total DKH2 energies were higher by more than 12 E_h but the values of r_e, ω_e, and IE$_e$ differed by just −0.0001 Å, −0.1 cm^{-1}, and −0.01 eV, respectively. Compared to DKH4 the total energy differed from DKH3 by more than 1.5 E_h but the differences in the spectroscopic constants were an order of magnitude smaller than the analogous DKH2−DKH3 results. Hence while the total energies exhibit dramatic differences from DKH2 to DKH4, the spectroscopic constants and energy differences are well-converged at DKH3 for these molecules.

Finally in order to investigate the effects of higher order electron correlation beyond the CCSD(T) level of approximation, CCSDT and CCSDTQ calculations[15] were carried out with triple- and double-ζ basis sets, respectively, with only valence electrons correlated. These results are also shown in Table 1. Compared to CCSD(T) with the same basis set, the CCSDT bond length is slightly shorter by 0.002 Å, the harmonic frequency increases by 6.1 cm^{-1}, and the IE is increased by just 0.005 eV. In the case of r_e and ω_e, inclusion of connected quadruple excitations in CCSDTQ nearly counteracts these effects but also slightly increases the IE by 0.003 eV. Adding up all of these corrections to our best CCSD(T) ECP values (neglecting spin−orbit effects, which were previously found[11] to be negligible for HfO), we end up with an estimate of 1.694 Å for r_e(HfO$^+$), 1.696 Å for r_0(HfO$^+$), 1022 cm^{-1} for ω_e (HfO$^+$), and 7.91 eV for IE(HfO). These results are in very good agreement with the experimental values of $r_0 = 1.687 \pm 0.003$ Å, $\omega_e = 1017.7 \pm 1.0$ cm^{-1}, and IE $= 7.91687 \pm 0.00010$ eV.[3] The underestimation of the IE in the previous CCSD(T) calculations of Merritt et al.,[3] which utilized an older PP and a polarized triple-ζ quality basis set, can now be seen to be due to an inadequate treatment of Hf 5*sp* correlation and in particular the lack of corrections for the pseudopotential approximation and 4f electron correlation.

3. Summary

In the present work a systematic treatment of both the basis set and correlation treatment has been carried out for the spectroscopic properties of the HfO$^+$ molecule. After extrapolation to the complete basis set limit, taking into account approximations due to the use of a pseudopotential treatment on Hf, and correlation of the low-lying 4f electrons, near quantitative agreement with recent experimental results for the spectroscopic constants of HfO$^+$ and the ionization energy of HfO have been obtained.

Acknowledgment. K.A.P acknowledges the support of the National Science Foundation under Grant No. CHE-0723997. J.M.M. and M.C.H. were supported by the U.S. Department of Energy under Grant No. DE-FG02-01ER15153-A005.

References and Notes

(1) Softley, T. P. *Int. Rev. Phys. Chem.* **2004**, *23*, 1.

(2) Heaven, M. C. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4497.

(3) Merritt, J. M.; Bondybey, V. E.; Heaven, M. C. *J. Chem. Phys.* **2009**, *130*, 144503.

(4) Merritt, J. M.; Han, J.; Heaven, M. C. *J. Chem. Phys.* **2008**, *128*, 084304.

(5) Goncharov, V.; Kaledin, L. A.; Heaven, M. C. *J. Chem. Phys.* **2006**, *125*, 133202.

(6) Goncharov, V.; Heaven, M. C. *J. Chem. Phys.* **2006**, *124*, 064312.

(7) Gibson, J. K.; Marcalo, J. *Coord. Chem. Rev.* **2006**, *250*, 776.

(8) Tyagi, R. *Ab initio studies of systems containing actinides using relativistic effective core potentials*; Ph.D. Thesis; Department of Chemistry, Ohio State University: Columbus, OH, 2005; Advisor, R. M. Pitzer.

(9) Rauh, E. G.; Ackermann, R. J. *J. Chem. Phys.* **1974**, *60*, 1396.

(10) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(11) Spohn, B.; Goll, E.; Stoll, H.; Figgen, D.; Peterson, K. A. *J. Phys. Chem. A*, in press.

(12) Figgen, D.; Peterson, K. A.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2009**, *130*, 164108.

(13) Douglas, M.; Kroll, N. M. *Ann Phys. (New York)* **1974**, *82*, 89. Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742. Jansen, G.; Hess, B. A. *Phys. Rev. A* **1989**, *39*, 6016.

(14) Reiher, M.; Wolf, A. *J. Chem. Phys.* **2004**, *121*, 2037. Reiher, M.; Wolf, A. *J. Chem. Phys.* **2004**, *121*, 10945. Wolf, A.; Reiher, M.; Hess, B. A. *J. Chem. Phys.* **2002**, *117*, 9215.

(15) Kállay, M.; Surján, P. R. *J. Chem. Phys.* **2001**, *115*, 2945. Kállay, M. MRCC, a string-based quantum chemical program suite, see also http://www.mrcc.hu.

(16) Dunham, J. L. *Phys. Rev.* **1932**, *41*, 721.

(17) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; et al. *MOLPRO*, Version 2008.1, a package of ab initio programs. http://www.molpronet.

(18) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219. Erratum, *J. Chem. Phys.* **2000**, *112*, 3106.

JP904936X