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An Anomalous Bond Angle in (116)H_2. Theoretical Evidence for Supervalent Hybridization

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The electronic structure and geometry of the superheavy group VI molecule (116)H_2 are examined and compared to those of the lighter group analogues H_2O−PoH_2. The spin−orbit interaction is found to lengthen the (116)−H bond and more importantly lead to a modest but significant H−(116)−H bond angle increase. It is suggested that the latter is the result of a rehybridization of the valence 7p orbitals with a “supervalent” 8s orbital of element 116.

Introduction

Based on concepts of hybridization and valence shell electron pair repulsion theory, the standard, introductory explanation for the near tetrahedral bond angle of water (∼104.5°) has proven successful and, despite its limitations, is widely accepted. Using the well-known language of valence bond theory, a mixture of valence s and p orbitals allows the construction of hybrids amenable to this relatively large H−O−H bond angle.[1] More complete discussions extend to the heavier group 6 dihydrides for which $\angle$(H−X−H) ranges from ∼92.1° in H_2S to ∼90.2° in TeH_2.[2] The abrupt decrease in the bond angle from O to S and smaller decreases from S to Te are generally taken as evidence that for the heavier atoms bonding involves contributions from nearly pure valence p orbitals. The group VI dihydride bond angle might therefore be understood as a proxy for the degree of s orbital participation (hybridization) extant in the bonding valence. It is interesting, then, that although our and others’ predictions of the experimentally unknown bond angle for PoH_2 conform to expectations for group VI dihydrides, our predictions for that of its superheavy analogue (116)H_2 do not.[3]

For obvious reasons, water is perhaps the most widely studied molecule. This and the fact that use of periodic analogy to explain molecular behavior is one of the most powerful predictive tools a chemist can employ motivate this work. In this contribution, we explore the extent to which the relevant analogies for XH_2 molecules pertain to this transactinide species at the frontier of the periodic table.[4] In particular, we seek to learn if the severe spin−orbit effects in element 116 have an impact on the electronic structure of its compounds that would call into question assumptions based on chemical periodicity. As it is extremely unlikely that molecules of element 116 will ever be experimentally characterized, the use of established theoretical methods provides the only near-term prospect that such a determination can be made.

Computational Details

All density functional and spin−orbit free ab initio geometry optimizations were performed using NWChem for which a spin−orbit DFT module and analytic gradients are available.[5] The DFT results reported here were obtained using the B3LYP hybrid density functional, and the ab initio results were obtained with coupled-cluster methods. Scalar relativistic effects were accounted for in all calculations through the use of shape-consistent effective core potentials for all group VI atoms.[6] Where indicated, spin−orbit effects were included through the use of spin−orbit operators associated with these RECPs. Spin−orbit coupling was included at the ab initio level using the two-component, Kramers’-restricted method available within the MOLFDIR package for which analytic gradients are not available.[7] In each of these cases, the minimum was located by applying a downhill simplex method to a potential energy surface interpolated from 88 single-point energies calculated near the equilibrium geometry.[8] Electronic transition energies for atomic element 116 were calculated using the multireference spin−orbit configuration interaction functionality of the COLUMBUS suite of programs.[9] Dunning’s cc-pVDZ basis set for hydrogen was used throughout whereas those for O, S, Se, and Te were published for use with the respective core potentials.[10] The Cartesian basis sets for Po and a more extensive one for element 116 were optimized separately and are available in the Supporting Information.

Results and Discussion

Results of these calculations are summarized in Table 1. At the ab initio coupled cluster and DFT/B3LYP levels of theory we find good agreement with available experimental bond length and bond angle data for H_2O to TeH_2. Though these molecules are not the focus of this contribution, it is comforting that the salient trends are reproduced. Importantly, but not surprisingly, the calculated results for these species are also relatively insensitive to the inclusion of spin−orbit coupling at DFT/B3LYP level. In polonium hydride, for which no experimental data are available, the bond angle is slightly less than 90°, continuing the trend seen in earlier chalcogen dihydrides. Spin−

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TABLE 1: Optimized Geometries for Group VI Dihydrides[a]

molecule	method		∠(H−X−H) (deg)	R(X−H) (Å)
$(116)H_2$	DFT/B3LYP	SO	94.73	2.047
	DFT/B3LYP		90.07	1.836
	KR−CCSD(T)	SO	94.70	2.059
	KR−CCSD	SO	94.22	2.051
	HF−CCSD(T)		89.11	1.824
	HF−CCSD		89.33	1.819
PoH_2	DFT/B3LYP	SO	89.36	1.808
	DFT/B3LYP		89.71	1.789
	HF−CCSD(T)		89.11	1.747
	HF−CCSD		89.30	1.744
TeH_2	DFT/B3LYP	SO	90.05	1.690
	DFT/B3LYP		90.05	1.690
	HF−CCSD(T)		90.15	1.655
	HF−CCSD		90.31	1.653
	expt		90.26	1.659
SeH_2	DFT/B3LYP	SO	91.18	1.467
	DFT/B3LYP		91.21	1.467
	HF−CCSD(T)		91.62	1.430
	HF−CCSD		91.73	1.430
	expt		90.57	1.460
H_2S	DFT/B3LYP	SO	92.78	1.352
	DFT/B3LYP		92.78	1.352
	HF−CCSD(T)		92.50	1.336
	HF−CCSD		92.62	1.335
	expt		92.12	1.336
H_2O	DFT/B3LYP	SO	105.10	0.971
	DFT/B3LYP		105.10	0.971
	HF−CCSD(T)		103.54	0.967
	HF−CCSD		104.53	0.967
	expt		104.52	0.957

[a] SO = calculation includes the spin−orbit interaction. DFT = based on density functional theory. KR = based on a Kramers'-restricted, two-component ab initio wave function. HF = based on a Hartree−Fock ab initio wave function. Experimental data are from ref 1.

TABLE 2: Mulliken Population Analyses Calculated at the DFT/B3LYP Level of Theory[a]

atom	valence s population	∠H−X−H (deg)
(116)	2.01 (1.93)	94.73
Po	1.96 (1.96)	89.36
Te	1.97	90.05
Se	1.79	91.18
S	1.78	92.78
O	1.55	105.10

[a] Data in parentheses exclude spin−orbit coupling and are included for comparison.

TABLE 3: Electronic Transitions in Element 116 Calculated at the Multireference Spin−Orbit Configuration Interaction Level[a]

state (parity)	primary (spinor) configuration	ΔE (eV)
$J = 2(+)$	$p^{*2}\,p^2$	0
$J = 0(+)$	$p^{*2}\,p^2$	1.243
$J = 2(-)$	$p^{*2}\,p^1\,s^1$	2.816
$J = 1(-)$	$p^{*2}\,p^1\,s^1$	4.600
$J = 1(+)$	$p^{*1}\,p^3$	7.989
$J = 2(+)$	$p^{*1}\,p^3$	8.611
$J = 0(+)$	p^4	11.216
	Without Spin−Orbit Coupling	
^3P	p^4	0
^1D	p^4	1.000
^1S	p^4	2.485
^5S	p^3s^1	3.399

[a] 6s and 6p electrons were designated inactive in all CI expansions. In this notation: $p^* = p_{1/2}$, $p = p_{3/2}$, the two spinor components of the 7p shell. The "s" refers to the 8s orbital of element 116.

orbit coupling does result, however, in a marginal (∼0.02 Å) elongation of the Po−H bond—the consequence of a moderate radial expansion of the $p_{3/2}$ spinor component of the polonium valence p shell.[3] In the absence of spin−orbit coupling, the calculated geometry for $(116)H_2$ is strikingly similar to that of PoH_2, exhibiting only a very slightly longer bond length and a nearly identical bond angle. With the inclusion of spin−orbit coupling, however, we see a dramatic but more or less expected increase in bond length (∼0.2 Å—again the result of the expansion of the valence $p_{3/2}$ spinor) and a sizable but unexpected increase in bond angle to nearly 95°. The results are again entirely consistent across the spectrum of theoretical methods used and invite the question of why the trend of decreasing bond angle among group VI dihydrides should be so severely disrupted that ∠(H−X-H) in $(116)H_2$ is second only to water.

These observations suggest that to some extent severe spin−orbit coupling in element 116 reorganizes the valence structure of the $(116)H_2$ molecule. If we take seriously even a qualitative relationship between bond angle and valence s orbital participation in bonding, then we must conclude that the incorporation of spin−orbit coupling into the treatment of $(116)H_2$ increases the s character of the bonding molecular orbitals. Our contention is that the only reasonable source of this increased s character is the unoccupied 8s orbital of element 116.

Several lines of reasoning lead to this conclusion: That in absence of spin−orbit coupling the $(116)H_2$ bond angle is unremarkable suggests it is not the valence 7s orbital of element 116, which is not directly affected by spin−orbit coupling, that is the cause of the anomaly. Indeed, such would be quite surprising in light of the relativistic stabilization of valence s orbital expected in such a heavy element. This enhanced stability, accounted for through the use of relativistic effective core potentials in *all* of our calculations, would tend to decrease the participation of the 7s electrons in bonding and isolate them as a nonbonding core-like lone pair. Though not necessarily definitive, the results of Mulliken population analyses given in Table 2 do demonstrate a steady increase in central atom valence s population that tracks the bond angle decline from H_2O to H_2Po and is itself insensitive to spin−orbit coupling. These data also indicate that, unlike in the lighter group VI dihydrides, the spin−orbit effect significantly *increases* the s population in $(116)H_2$. Because the 7s orbital of element 116 is only indirectly affected by spin−orbit effects and because population analyses such as these are unable to distinguish between them, we are comfortable in concluding that the spin−orbit induced population increase owes to a bleeding of electron density into the 8s shell. Under the C_{2v} double group symmetry necessary to describe spin−orbit coupling in these molecules, the s and all of the p orbitals span the same representation, allowing them to mix more freely than in its absence where orthogonality is required between s and two of the three valence p orbitals. (We should note that without spin−orbit coupling there is a small and somewhat counterintuitive decrease in s orbital population from PoH_2 to $(116)H_2$. The source of this marginal decrease is not clear but we believe that it is unimportant and likely owes from differences in the respective central atom basis sets.)

Furthermore, the data in Table 3 indicate that electronic transitions from the $7p_{3/2}$ spinor to the 8s shell in atomic element 116 occur at energies actually *lower* than those among the $7p_{1/2}$ and $7p_{3/2}$ spinor components of the 7p shell. Similar behavior has been predicted for other transactinides and suggests that the combination of spin−orbit and shell-structure relativistic effects does indeed put the 8s shell in energetic proximity to the valence of these atoms.[11]

Finally, DFT calculations done using a restricted or minimal s orbital basis set (i.e., with diffuse s functions removed) exhibit

TABLE 4: Geometry Optimizations of (116)H_2 Using a Full and Restricted Cartesian Basis Set[a]

method		∠(H−X−H)	R(X−H) (Å)
Full 5s7p6sd2f Basis Set			
DFT/HF-exch[b]	SO	98.33	2.058
DFT/HF-exch		90.50	1.808
DFT/B3LYP	SO	94.73	2.047
DFT/B3LYP		90.07	1.836
Minimal s-Space7p5sd2f Basis Set			
DFT/HF-exch	SO	93.85	2.018
DFT/HF-exch		90.11	1.796
DFT/B3LYP	SO	92.38	2.019
DFT/B3LYP		89.82	1.824

[a] SO = calculation includes the spin−orbit interaction. DFT = based on density functional theory. [b] In addition to data for the B3LYP hybrid energy density functional, results using the Hartree−Fock exchange only density functional are reported. Use of this functional is essentially equivalent to the corresponding HF−SCF or KR−SCF techniques.

a much more modest bond angle increase upon the inclusion of spin−orbit interaction (Table 4). If one were to argue that the bond angle increase owes principally to some feature of the $7p_{1/2}/7p_{3/2}$ valence spinors, then it should not have been significantly affected by this restriction just as the calculated spin−orbit bond lengthening was not. If on the other hand, 8s participation is important to the geometry of (116)H_2, then minimizing the flexibility of the s-space would indeed be expected to impact the result, as it has.

Conclusion

At first glance, it may seem that a great deal is being made of a bond angle that is merely ∼5° greater than one might expect. Aside from the absolute magnitude of this change, however, it is clear that the valence electronic structure of (116)H_2 is different from that of all of the other group VI hydrides and its geometry represents a notable departure from established periodic trends. The differences are shown to be the result of severe spin−orbit coupling that reorganizes the valence space of element 116 and has the effect of causing a significant increase in both the central atom−hydrogen bond length and bond angle. In some respects, namely the importance of valence hybridization, the severe relativistic spin−orbit effects that we suggest allow the supervalent 8s orbital to enter the valence space, which makes element (116)H_2 more similar to water than any of the other XH_2 molecules. This ps (as opposed to sp) supervalent hybridization scheme might prove to be important as well to other aspects of transactinide chemistry, particularly those of the 7p block. Such has been suggested in previous work, but the evidence presented here is perhaps the most compelling yet in making the case that atomic orbitals beyond what would normally be considered to be valence have a measurable effect on the chemistry of superheavy elements.[11−13]

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Supporting Information Available: Cartesian basis sets used for element 116 and polonium. Extended version of Table 1 listing optimized geometries obtained from additional computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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