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Spin−Orbit Effects on the Electronic Structure of Heavy and Superheavy Hydrogen Halides: Prediction of an Anomalously Strong Bond in H[117]

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The bond lengths, vibrational frequencies, and bond dissociation energies of the heavy and superheavy hydrogen halides HBr, HI, HAt, and H[117] ([117] = element 117) have been calculated by using multireference relativistic configuration interaction (MR-RCI) and coupled-cluster [CCSD(T)] electronic structure methods. The effects of spin−orbit coupling on the coupled-cluster calculations were approximated by adding a correction term that represents the spin−orbit effect on the energy in the MR-RCI calculations. The calculated values are in good accord with the available experimental and theoretical data for HBr, HI, and HAt, with the latter predicted to have a bond length of 1.74 Å and a dissociation energy of 2.27 eV via the corrected CCSD(T) calculations. By using the same method, H[117] is predicted to have a bond length of 1.94 Å, a vibrational frequency of 1648 cm^{-1}, and a dissociation energy of 2.21 eV; i.e., it is predicted to have a significantly longer but only marginally weaker bond than HAt. This prediction is explained via strong spin−orbit effects, which cause the 8s orbital of [117] to be involved in the bonding.

Introduction

The 1990s have seen renewed interest in the chemistry of the superheavy elements, which are nominally those with atomic number greater than 100.[1] There are two primary reasons for this increased interest. First, due to the efforts of scientists at the GSI, Darmstadt, the number of known elements has increased to 112.[2] Second, the controversy over the naming of element 106 (seaborgium) served to increase the awareness of the chemistry of the superheavy elements in the chemical community.[3] Because only a few atoms of these elements are generally produced at any one time, and because they are very short-lived, much of the research on the properties of the known and unknown superheavy elements has involved theoretical methodologies and predictions.[4] Pershina has provided an excellent review of the use of electronic structure theory to describe and predict the chemistry of the transactinide elements.[5]

If synthesized, element 117 is expected to occupy a position in the periodic table among the halogen elements, having two valence s and five valence p electrons or, alternatively, one valence p-hole. Inasmuch as the hydrogen halides are perhaps the most extensively studied molecular systems from both experimental and theoretical perspectives, it is of interest to consider the electronic structure of the superheavy hydrogen halide H[117] vis-à-vis its well-known cousins.[6] In particular, we are interested in exploring whether the properties of H[117] are affected by the severe relativistic effects[7] that would be expected in element 117. Some of these issues have been recently discussed by Saue et al. in their single-configuration Dirac−Hartree−Fock (DHF) calculations on HI, HAt, and H[117].[8] In this contribution, we will report correlated relativistic electronic structure calculations on H[117] and will predict its bond length, vibrational frequency, and bond dissociation energy. We will consider both relativistic shell effects and spin−orbit effects in our calculations and will compare our results to the available experimental data.

Theoretical Methodologies

Electronic structure calculations have been carried out on the hydrogen halides HX (X = Br, I, At, [117]) and their constituent atoms; the lightest hydrogen halides, HF and HCl, were not investigated in order to avoid complications arising from the explicit treatment of differing numbers of valence electrons (F and Cl have no occupied d orbitals). Because of the importance of including both the scalar and spin−orbit relativistic effects and of the desirability of reporting size-consistent calculations, we have used and combined the results of two different correlated methods. First, we used the multireference relativistic configuration interaction (MR-RCI) approach with relativistic effective core potentials (RECPs),[9,10] a method that allows for the explicit inclusion (or exclusion) of a spin−orbit potential. For each HX molecule, the $(n-1)$d, $(n-1)$s, $(n-1)$p, ns, and np orbitals were included in the valence space, which allowed the use of a common reference space, set of configurations, RECP size, and basis set contraction scheme for all of the molecular species examined. Despite the fact that common bonding models consider the filled $(n-1)$s, $(n-1)$p, and $(n-1)$d shells to be nonbonding, these "outer core" orbitals were explicitly treated in the valence set in order to minimize errors resulting from core-valence polarization.[11] Because a common valence space was used for all of the molecules studied, variations among the HX molecules are more clearly attributable to actual physical effects rather than unphysical errors resulting from differences in the core-valence partition.

The basis set used for the halogen atoms consists of (6sd6p1fp) Cartesian primitives contracted to [6sd4p1fp] varia-

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tional functions. The exponents of the f polarization functions were chosen to maximize radial overlap with the $(n - 1)$d functions and were 6.02, 2.47, 1.67, and 1.21 for Br, I, At, and [117], respectively. The hydrogen basis set contraction scheme was (4s3p)/[3s2p]. We have previously published the RECP for [117].[10e]

The reference space used for the MR-RCI calculations consisted of single and double excitations from the $X(ns^2\pi^4\sigma^2)$, $X(ns^2\pi^4\sigma^1\sigma^{*1})$, $X(ns^2\pi^3\sigma^2\sigma^{*1})$, $X(ns^2\pi^3\sigma^1\sigma^{*2})$, and $X(ns^2\pi^4\sigma^{*2})$ configurations. This procedure leads to a CI space consisting of 22 200 determinants and 44 290 double-group functions and including all of the important configurations at all bond lengths, both with and without spin−orbit coupling. For practical reasons, excitations to the d-shell were excluded from the reference space. This exclusion does result in small core-valence correlation errors that manifest themselves primarily as bond lengths that are ∼0.02−0.04 Å too long at the MR-CISD level. These errors are fairly constant, however, and do not affect the conclusions of the study.

As in other applications of configuration interaction methods, in the absence of a full CI the MR-RCI method suffers from size consistency errors.[12] These errors are expected to be more problematic in the calculation of the molecular properties of the HX molecules than in the calculation of atomic properties. No attempt is made here to correct for size-consistency through the use of *a posterori* corrections to the CI wavefunction, such as the Langhoff−Davidson formula.[13] Nevertheless, the extensive reference space used and the choice of parallel valence orbitals and configuration sets among the different HX molecules are expected to minimize size-consistency errors and lead to meaningful comparisons among the properties calculated for the series of molecules.

In order to address the size-consistency and core-valence correlation problems in the MR-RCI calculations more directly, we also calculated the electronic structure of the HI, HAt, and H[117] molecules by using the coupled-cluster method with singles, doubles, and noniterative triples [CCSD(T)].[14] This method is implicitly size-consistent and generally gives results that are in excellent accord with experiment.[15] The CCSD(T) calculations were carried out by using the ACES II package[16,17] and employing the same basis sets and effective core potentials that were used in the MR-RCI calculations. In the coupled-cluster calculations, all 26 valence electrons were correlated and hence core-valence correlation is included to the greatest possible extent.

This implementation of the CCSD(T) method does not allow for the explicit inclusion of spin−orbit effects. In order to approximate the effects of spin−orbit coupling on the CCSD(T) energy at each bond length r, we have added a correction term, ΔE^{SO}, defined as the difference in the MR-RCI energies calculated with $(E_{RCI}{}^{SO})$ and without $(E_{RCI}{}^{NOSO})$ the inclusion of the spin−orbit potential:

$$\Delta E^{SO}(r) = E_{RCI}{}^{SO}(r) - E_{RCI}{}^{NOSO}(r)$$

By combining the size-consistent CCSD(T) calculations with the spin−orbit corrections from the RCI calculations, we are left only with the small size-consistency errors stemming from the evaluation of the spin−orbit operator.

The potential energy surface for each molecule was determined via single-point calculations. Energies were evaluated at every 0.1 Bohr within ±0.5 Bohr of R_e; a coarser grid of points was chosen for distances farther from the minimum. R_e and ω_e were evaluated by fitting the single-point calculations to a fifth-order polynomial. We estimate that the error in determining R_e by this fitting procedure is ±0.001 Å. The dissociation energy D_e was determined as the energy difference between R_e and at an asymptotic limit, defined as a bond length for which the energy was essentially invariant ($\Delta E < 0.005$ Hartree/Bohr). This limit was achieved at bond lengths of 7−10 Å for the molecules studied. The use of an asymptotic limit, rather than separated atoms, allowed for an even-handed treatment of configuration interaction in the RCI calculations. Test calculations at a bond length of 50 Å verified that the asymptotic limit had been achieved.

TABLE 1: Calculated and Experimental Values for the Bond Lengths (R_e), Vibrational Frequencies (ω_e), and Bond Dissociation Energies (D_e) of HBr, HI, HAt, and H[117], Calculated at the MR-RCI and CCSD(T) Levels without [MR-RCI(noso) and CCSD(T)] and with [MR-RCI and CCSD(T) + ΔE^{SO}] Spin−Orbit Coupling

molecule	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
	HBr		
MR-RCI	1.429	2692	4.17
expt (ref 18)	1.414	2650	3.92
	HI		
MR-RCI(noso)	1.646	2166	3.18
MR-RCI	1.648	2189	2.93
CCSD(T)	1.631	2302	3.13
CCSD(T) + ΔE^{SO}	1.634	2261	2.88
expt (ref 18)	1.609	2310	3.20
	HAt		
MR-RCI(noso)	1.739	2010	2.85
MR-RCI	1.779	1803	2.24
CCSD(T)	1.707	2203	2.88
CCSD(T) + ΔE^{SO}	1.737	2029	2.27
expt (ref 21)			2.52 ± 0.17
	H[117][a]		
MR-RCI(noso)	1.833	1893	2.76
MR-RCI	1.968	1569	2.21
CCSD(T)	1.803	1972	2.78
CCSD(T) + ΔE^{SO}	1.938	1648	2.21

[a] An atomic mass of 302 u was assumed for [117].

Results and Discussion

The calculated MR-RCI and spin−orbit corrected CCSD(T) bond lengths (R_e), vibrational frequencies (ω_e), and dissociation energies (D_e) for the HX molecules are presented in Table 1, along with the available experimental values. The values of R_e and D_e are plotted in Figures 1 and 2. As seen in Figure 1, the general trend in the experimental bond lengths of the hydrogen halides is a nearly linear increase in equilibrium bond length with increasing period number.[18] The exception occurs at HF, which has an unusually short bond as a result of the well-known tendency for the first shell of each symmetry to be more energetically stable and radially compact than later shells (the primogenic effect). This trend in bond length is reproduced quite well in both the relativistic configuration interaction and coupled-cluster results.

In order to examine the influence of spin−orbit coupling on the calculated bond lengths of HI, HAt, and H[117], we also report in Table 1 the results of MR-RCI calculations with the exclusion of spin−orbit effects [RCI(noso)] and the CCSD(T) results without correction by ΔE^{SO}. These data clearly show the expected bond length increase due to spin−orbit effects, and as expected, this lengthening becomes more significant as the halogen atom becomes heavier. For H[117], both the MR-RCI and CCSD(T) methods predict that the bond length increases by ≥0.1 Å because of spin−orbit effects, a result comparable to that observed by Saue et al. in their nonrelativistic

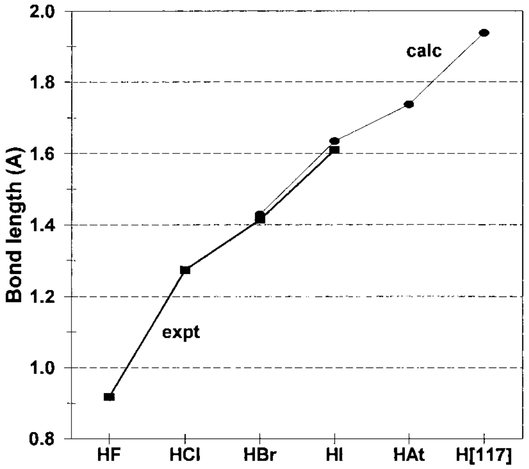

Figure 1. Comparison of experimental (■) and calculated CCSD(T) + ΔE^{SO} (●) values of the equilibrium bond length R_e (Å) for the hydrogen halides. The MR-RCI calculated bond length for HBr is also included in the graph.

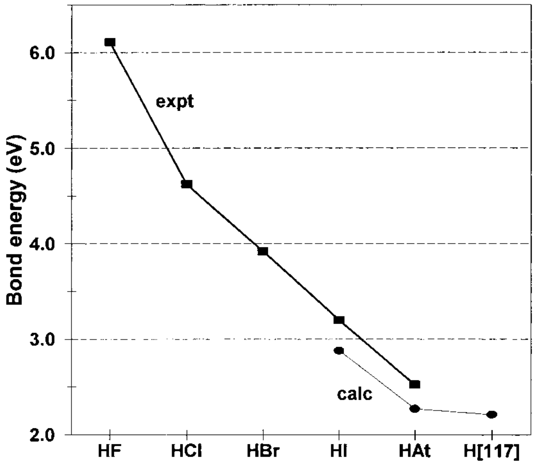

Figure 2. Comparison of experimental (■) and calculated CCSD(T) + ΔE^{SO} (●) values of the dissociation energy D_e for the hydrogen halides.

and relativistic Hartree−Fock calculations on H[117].[8] Our MR-RCI calculated values for the bond length for H[117], 1.968 Å, is very similar to that predicted from the DHF calculations of Saue et al. (1.978 Å), and our calculated MR-RCI vibrational frequency for H[117] (1569 cm^{-1}) is also similar to their DHF value (1531 cm^{-1}). Those authors did not specify their assumed atomic mass of [117], but it is likely that it is close to the 302 u assumed here. The spin−orbit corrected CCSD(T) calculations predict a somewhat shorter H−[117] bond (1.938 Å) and a correspondingly higher vibrational frequency (1648 cm^{-1}).

The calculated bond length in H[117] is perhaps slightly longer than would be predicted on the basis of a simple linear extrapolation of the experimental R_e values for the lighter hydrogen halides. This observation has also been made by Saue et al. and has a rather straightforward explanation.[8] The large spin−orbit splitting of the ^2P term of [117] results in spatial and energetic separation of the lower-energy $7p_{1/2}$ spinor, which largely precludes participation of this spinor in molecular bonding interactions. Spin−orbit coupling thus essentially leads to an additional, nonbonding orbital that contributes another repulsive interaction and thereby lengthens the bond. A complementary explanation for the spin−orbit bond lengthening relies again on the observation that the $7p_{3/2}$ spinor, which is principally involved in the H−[117] bond formation, has a greater radial extent than the spin−orbit averaged 7p orbital. The spin−orbit induced bond length increases for HAt (~0.01−0.02 Å) and HI (<0.01 Å) are predictably more modest than for H[117] because of the much smaller spin−orbit coupling, although the spin−orbit splitting of the ^2P term in At (~2.9 eV) is still quite substantial.

The near-linear increase in R_e with period number is matched by a near-linear decrease in bond dissociation energies with increasing period number for HF−HAt (Figure 2). Again, an exception occurs for HF, which has an unusually strong bond as a result of the same effect discussed in the context of bond lengths. The linear trend toward decreasing values of D_e is reproduced at both the MR-RCI and CCSD(T) levels, both with and without spin−orbit coupling. The spin−orbit effects decrease the calculated value of D_e for HI and HAt, as expected from the observation that spin−orbit coupling makes bonding orbitals less bonding and antibonding orbitals less antibonding.

The results for the bond lengths and bond dissociation energies of HI and HAt are in reasonable accord with the available experimental data and with previous theoretical values. For HI, the calculated bond length is 0.04 Å too long and the spin−orbit corrected CCSD(T) dissociation energy of HI is too low by 0.27 eV. Currently, very little is known about HAt, but our calculated bond length of 1.737 Å and dissociation energy of 2.27 eV are nearly identical to the values calculated by Visscher et al., who found $D_e = 2.28$ eV and $R_e = 1.739$ Å.[19] Dolg et al. calculate somewhat different constants for HAt, but the values are still generally concurrent, $D_e = 2.61$ eV and $R_e = 1.73$ Å.[20] These calculated values for D_e in HAt bracket the experimental estimate by Grover et al., namely $D_{300} = 2.52 \pm 0.17$ eV.[21]

We have applied the same methodologies that lead to good results for the bond dissociation energies in HI and HAt to calculate the same property for H[117]. Interestingly, the bond dissociation energy of H[117] does not follow the nearly linear trend of decreasing D_e with increasing period of X. With and without spin−orbit coupling, the bond in H[117] is predicted to be only marginally weaker than that in HAt (Table 1). Both the MR-RCI and spin−orbit corrected CCSD(T) methods give values of D_e for H[117] that are only a few tenths of an electronvolt lower than that of HAt. This anomalous behavior occurs because the spin−orbit induced decrease in the bond dissociation energy in H[117] is actually slightly smaller than that in HAt. This finding that spin−orbit coupling decreases the bond strength in H[117] less than it does so in HAt is surprising, especially in light of the large spin−orbit splitting of the ^2P term of [117] ($P_{3/2}-P_{1/2} \sim 8.6$ eV) relative to that in At (~2.91 eV) or I (~0.94 eV). As noted above, an increase in the spin−orbit splitting of this term would be expected to lead to a dramatic decrease in the bond dissociation energy, so the explanation of this peculiar observation lies elsewhere.

We believe that the unusual moderation in the effect of spin−orbit coupling on the bond dissociation energy of H[117] occurs *because* of the strong spin−orbit splitting rather than in spite of it. The severe splitting of the 7p orbitals, in conjunction with the scalar relativistic stabilization of s orbitals, serves to increase the importance of the 8s orbital in consideration of the H−[117] bonding. Invoking the relativistically stabilized 8s orbital is not a new notion: Kaldor et al. have used relativistic coupled cluster calculations to predict that stabilization of the 8s orbital is significant enough to allow the superheavy noble gas [118] to have a small electron affinity,[22] making [118] unique among the noble gases. We see a similar effect in RCI calculations on atomic [117]. Table 2 presents the lowest atomic electronic transition energies of I, At, and [117], calculated with the RCI

TABLE 2: Relative Energies of the Electronic States (Indexed by *J* and Parity under *jj*-Coupling) of I, At, and [117] As Calculated by Using the Relativistic Configuration Interaction Method with Double (RCI-dd), Single (RCI-d), and No (RCI-nod) d Excitations Allowed

J	relative energy (eV)			
(parity)	RCI-dd	RCI-d	RCI-nod	principle configuration
		I		
$^3/_2$ (−)		0.0	0.0	$5s^25p_{1/2}{}^25p_{3/2}{}^3$
$^1/_2$ (−)		0.936	0.812	$5s^25p_{1/2}{}^15p_{3/2}{}^4$
	exptl (ref 23): 0.925 eV			
		At		
$^3/_2$ (−)	0.0	0.0	0.0	$6s^26p_{1/2}{}^26p_{3/2}{}^3$
$^1/_2$ (−)	2.913	2.957	2.965	$6s^26p_{1/2}{}^16p_{3/2}{}^4$
	calcd (ref 20a): 2.709 eV			
		[117]		
$^3/_2$ (−)	0.0	0.0	0.0	$7s^27p_{1/2}{}^27p_{3/2}{}^3$
$^5/_2$ (+)		4.708	4.844	$7s^27p_{1/2}{}^27p_{3/2}{}^2(j_1 = 2)8s^1(j_2 = {}^1/_2)$
$^3/_2$ (+)		5.716	5.778	$7s^27p_{1/2}{}^27p_{3/2}{}^2(j_1 = 2)8s^1(j_2 = {}^1/_2)$
$^1/_2$ (+)		6.510	6.566	$7s^27p_{1/2}{}^27p_{3/2}{}^2(j_1 = 0)8s^1(j_2 = {}^1/_2)$
$^1/_2$ (−)	8.642	8.936	6.742	$7s^27p_{1/2}{}^17p_{3/4}{}^4$

method with varying degrees of excitation from the d orbitals. For I and At, the lowest excitation corresponds to the spin−orbit transition between the states derived from the ^2P term, i.e., transitions that correspond to excitation of an electron from the $np_{1/2}$ to the $np_{3/2}$ spinor. For [117], the splitting of the ^2P term is so great that this spin−orbit transition is predicted to occur at >8 eV. At lower energy are transitions that correspond to excitation from the $7p_{3/2}$ spinor to the $8s_{1/2}$ spinor, implying that it requires less energy to promote an electron from the $7p_{3/2}$ to the $8s_{1/2}$ spinor than to promote an electron from the $7p_{1/2}$ to the $7p_{3/2}$ spinor! Thus, the spin−orbit effects in [117] destabilize and expand the $7p_{3/2}$ spinor relative to the 7p spin−orbit average to such an extent that contributions of the 8s orbital to molecular interactions become energetically favorable. Put another way, the destabilization of the $7p_{3/2}$ spinor makes it amenable to the formation of a ps (as opposed to sp) hybrid with a relativistically stabilized 8s shell. This conclusion is supported by an analysis of the H[117] RCI wavefunction, which shows that the first molecular excited state at the asymptotic limit is best described as $H(^2S_{1/2}) + 117$ ($J = {}^5/_2{}^+$). This asymptote contrasts to the $H(^2S_{1/2}) + X$ ($J = {}^3/_2{}^-$, $^2P_{1/2}$) asymptotic limit exhibited by HAt and HI.

Further evidence for the participation of the 8s orbital of [117] is found in an analysis of the RCI natural orbitals (NOs) of the spin−orbit ground states of the HX molecules at their calculated equilibrium bond distances. The population of the σ^* NO of H[117] increases from 0.072 to 0.304 upon the inclusion of the spin−orbit effects. The corresponding NO population increases for HAt and HI are 0.059 to 0.121 and 0.051 to 0.058, respectively. In addition, the $(n + 1)$s character of this NO increases substantially from HI to H[117], to such an extent that in the latter this NO is probably best described as a ps hybrid. Because this is a natural orbital, i.e., an eigenfunction of the first-order reduced density matrix, this spin−orbit induced population increase represents a buildup of electron density in the interatomic region rather than a fortification of an energetically unfavorable antibonding interaction. Interestingly, the characters of the natural orbitals are not dramatically different in the absence of spin−orbit coupling. However, spin−orbit coupling is required to allow the significant occupation of this NO, which supports the interpretation that the $7p_{3/2}$ spinor is rather polarizable and in energetic and spatial proximity to the 8s shell. In short, spin−orbit coupling in H[117] allows and facilitates the transfer of electron density to the 8s orbital, which mitigates the bond destabilizing effect of the large $7p_{1/2}-7p_{3/2}$ splitting. The 8s orbital essentially assumes the role that the $7p_{1/2}$ spinor relinquishes by virtue of its large energetic separation from the bonding regime. It is worthwhile to note that the energetic separation of the 8s and $7p_{3/2}$ spinors in [117] is only slightly larger than that between the $6p_{1/2}$ and $6p_{3/2}$ spinors in At.

In summary, we have used correlated relativistic electronic structure calculations to predict that the severe spin−orbit coupling expected for [117] will cause H[117] to have a bond that is both unusually long and unusually strong. We are continuing to explore the effects of strong spin−orbit coupling on the structures and properties of compounds of the superheavy elements.

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References and Notes

(1) Seaborg, G. T.; Loveland, W. D. *The Elements Beyond Uranium*; Wiley-Interscience: New York, 1990.

(2) (a) Hofmann, S.; Ninov, V.; Hessberger, F. P.; Armbruster, P.; Folger, H.; Muenzenberg, G.; Schoett, H. J.; Popeko, A. G.; Yeremin, A. V. *Z. Phys. A: Hadrons Nucl.* **1996**, *354*, 229. (b) Armbruster, P. *Bull. Soc. Fr. Phys.* **1996**, *107*, 6.

(3) (a) Freemantle, M.; Dagani, R. *Chem. Eng. News* **1994**, October 10, 4−5. (b) Dagani, R. *Chem. Eng. News* **1997**, March 17, 10−11.

(4) See, for example: Jacoby, M. *Chem. Eng. News* **1998**, March 23, 48−54.

(5) Pershina, V. *Chem. Rev.* **1996**, *96*, 1977.

(6) Nomenclature: We will use [117] as the atomic symbol of element 117.

(7) Reviews of relativistic effects: (a) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. (b) Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276. (c) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719. (d) Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1. (e) Balasubramanian, K. *Relativistic Effects in Chemistry, Part A: Theory and Techniques*; Wiley-Interscience: New York, 1997.

(8) Saue, T.; Faegri, K.; Gropen, O. *Chem. Phys. Lett.* **1996**, *263*, 360.

(9) (a) Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J. G. *Int. J. Quantum Chem. Symp.* **1989**, *22*, 149. (b) Ermler, W. C.; Ross, R. B.; Christiansen, P. *A. Adv. Quantum Chem.* **1988**, *19*, 139.

(10) (a) Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3061. (b) Pitzer, R. M.; Winter, N. W. *Int. J. Quantum Chem.* **1991**, *40*, 773. (c) Chang, A.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500. (d) Chang, A.; Pitzer, R. M. Programs: ARGOS, CNVRT, SCFPQ, LSTRN, CIDBG. (e) Nash, C. S.; Bursten, B. E.; Ermler, W. C. *J. Chem. Phys.* **1997**, *106*, 5133.

(11) Schwerdtfeger, P.; Szentpaly, L.; Vogel, K.; Silberbach, H.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1986**, *84*, 1606.

(12) Martin, J. M. L.; Francois, J. P.; Gijbels, R. *Chem. Phys. Lett.* **1990**, *172*, 346.

(13) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(14) (a) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697. (b) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.

(15) (a) Watts, J. D.; Bartlett, R. J. *Int. J. Quantum Chem.* **1994**, *S28*, 195. (b) Oliphant, N.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *100*, 6550.

(16) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem.* **1992**, *S26*, 879.

(17) Stanton, J. F.; Gauss, J.; Watts, J. D; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K.-K.; Sekino, H.; Rozyczko, P.; Huber, C.; Bartlett, R. J. ACES II Program, Quantum Theory Project, University of Florida.

(18) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Molecular Spectra and Molecular Structure, Vol. 4; Van Nostrand Reinhold: New York, 1979. The values of D_e were calculated from the experimental values of D_0 and ω_e: $D_e = D_0 + {}^1/_2\hbar\omega_e$.

(19) Visscher, L.; Styszyñski, J.; Nieuwpoort, W. C. *J. Chem. Phys.* **1996**, *105*, 1987.

(20) (a) Dolg, M. *Mol. Phys.* **1996**, *88*, 1645. (b) Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H.; Schwerdtfeger, P. *Mol. Phys.* **1991**, *74*, 1265.

(21) Grover, J. R.; Malloy, D. E.; Mitchell, J. B. A. *J. Chem. Phys.* **1982**, *76*, 362.

(22) Eliav, E.; Kaldor, U.; Ishikawa, Y.; Pyykkö, P. *Phys. Rev. Lett.* **1996**, *77*, 5350.

(23) Moore, C.E. *Natl. Bur. Stand U.S. Circ. No. 467*; U.S. Government Printing Office: Washington, DC, Vol. I (1949), Vol. II (1952), Vol. III (1958).