levels and have minimal participation in overall π-bonding schemes.

The fact that the Xα calculations provided such a close match between the observed and calculated optical trends for the tricarbonyls of copper and silver, that they provided a clear picture of the differences in the electronic structures of gold dicarbonyl and its isocarbonyl isomer (thereby giving a more reasonable interpretation of the infrared and ultraviolet–visible spectra than previously possible), and that they helped to yield a simplified view of the bonding schemes in these complexes, in which the "anomalous" force constant trend observed experimentally could be rationalized, all attest to the usefulness and accuracy of the SCF–Xα–SW method as a predictive tool.

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Registry No. Cu(CO), 55979-21-0; $Cu(CO)_2$, 55979-20-9; $Cu(CO)_3$, 55979-19-6; Ag(CO), 59751-30-3; $Ag(CO)_2$, 59751-29-0; $Ag(CO)_3$, 58832-57-8; Au(CO), 60594-88-9; $Au(CO)_2$, 60594-90-3; (OC)Au(OC), 60582-72-1; Ni(CO), 33637-76-2; $Ni(CO)_2$, 33637-77-3; $Ni(CO)_3$, 26024-55-5; $Ni(CO)_4$, 13463-39-3.

Supplementary Material Available: Listings of partial wave analyses for spin-restricted SCF–Xα–SW calculations of M(CO) (M = Cu, Ag, Au) (Appendix I), of $M(CO)_2$ (M = Cu, Ag) (Appendix II), of $M(CO)_3$ (M = Cu, Ag) (Appendix III), and of (OC)Au(CO) and (OC)Au(OC) (Appendix IV) (52 pages). Ordering information is given on any current masthead page.

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Molecular Orbital Theory of the Properties of Inorganic and Organometallic Compounds. 2. STO-*N*G Basis Sets for Fourth-Row Main-Group Elements

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Extension of the STO-3G minimal basis set to the main-group fourth-row elements (Rb, Sr, In–Xe) has been proposed. Equilibrium geometries, calculated for a wide variety of simple molecules containing these elements, have been found to be in reasonable accord with the available experimental structural data.

Introduction

Ab initio molecular orbital calculations on molecules comprising only hydrogen and first-row atoms occupy a voluminous portion of the present-day chemical literature. Numerous also are applications of the theory to systems incorporating second-row elements. Far less attention has been given to molecules containing third-row atoms and even less so to compounds with still heavier elements. Most ab initio calculations on molecules incorporating fourth-row or higher elements have dealt only with diatomic or triatomic species. Straub and McLean[1] employed a minimal Slater basis set supplemented by polarization functions to determine the equilibrium bond distances in HI, IF, ICl, IBr, and I_2. The theoretical quantities were found to be in close agreement with their respective experimental values. Double-ζ-type basis sets have been used in calculations on rubidium fluoride,[2a,c] strontium oxide,[2b] and rubidium oxide.[3] Here, experimental geometries were assumed. An even more extensive calculation on RbF was performed by Matcha,[4] again assuming the experimental equilibrium geometry. Here a double-ζ-type basis set was augmented by p-, d-, and f-type functions on rubidium and d- and f-type orbitals on fluorine. Bagus, Liu, Liskow, and Schaefer[5] have reported a dissociation energy and equilibrium geometry for the hypervalent XeF_2 molecule, obtained with the use of a double-ζ-type Slater basis set, supplemented by polarization functions and various levels of configuration interaction. All levels of theory employed yielded equilibrium bond lengths in good agreement with the experimental value. The XeF bond dissociation energy was not, however, found to be well reproduced unless fairly high levels of configuration interaction were introduced. Earlier calculations by these same authors on the XeF molecule[6] indicated that this species probably was not significantly bound in the gas phase. Basch, Moskowitz, Hollister, and Hankin[7] have carried out single calculations (using experimental geometries) on XeF_2, XeF_4, and XeF_6 using a Gaussian basis set of split-valence type. The properties of these hypervalent species have been discussed in terms of their results.

Several publications have appeared in which minimal Slater-type or equivalent Gaussian basis sets have been employed for calculations on molecules containing fourth-row elements. Ungemach and Schaefer[8] obtained an equilibrium bond distance of 1.61 Å for HI using a multiconfigurational SCF procedure, in excellent agreement with the experimental value of 1.609 Å. An equilibrium bond of 1.56 Å was determined by Kubach and Sidis[9] for the XeH^+ molecule. Rode[10] has performed single calculations on HI and IF molecules, as well as on the hypervalent species, IF_3, IF_5, IO_2F, IOF_3, and IO_2F_3 and their associated anions and cations. His work employed a very small Gaussian-type basis set and utilized experimental

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or assumed equilibrium geometries.

A number of investigations have proceeded with the use of one-center expansion techniques. Where applicable, these are considerably less costly computationally than conventional methods which require the evaluation of multicenter integrals. Using a one-center approach, Mackrodt[11] performed relativistic Hartree–Fock calculations on a number of the simple hydrides of fourth-row elements. The reported theoretical equilibrium geometries are, however, generally in poor agreement with experiment. Hartmann, Papula, and Strehl[12] have obtained an equilibrium bond length for the tetrahedral SnH_4 molecule using a one-center expansion of a minimal Slater-type basis set. As with Mackrodt's calculation, it is in rather poor accord with the experimental value. On the other hand, the calculated bond length for the diatomic InH, obtained by Pyykko and Desclaux using a similar level of theory,[13] is in good agreement with the respective experimental quantity.

Another approach which has been employed in order to effect reduction in computation time is the use of effective potentials. Here, only valence orbitals are considered explicitly in the calculation, the inner-shell descriptions being replaced by a potential energy term in the one-electron Hamiltonian. Effective potential calculations have been reported by Kahn, Baybutt, and Truhlar[14] for the HI and I_2 molecules. The calculated bond lengths (1.622 and 2.766 Å, respectively) and bond dissociation energies (62 and 18 kcal mol^{-1}, respectively) are in relatively good agreement with experimental values (1.581 and 2.621 Å and 74 and 36 kcal mol^{-1}, respectively).

While a significant number of applications of nonempirical molecular orbital theory to the properties of molecules containing fourth-row elements have been carried out, no single level of theory has as yet been uniformly applied over a wide enough variety of such compounds to enable a broad assessment of its overall capabilities to be made. It is our purpose in the present study to do just this. Specifically, we have extended the previously defined STO-3G minimal basis sets[15] to the main-group elements of the fourth row. This level of nonempirical theory is relatively inexpensive computationally, so as to enable applications to a wide variety of moderately complex molecules, given presently available computational resources. In addition, and equally important, our previous experience with STO-3G representations for lighter elements, in particular with regard to the calculation of molecular equilibrium geometries, strongly suggests the ability of the simple method to perform to an adequate standard as to be of some use as a predictive tool.

Methods

STO-3G minimal basis sets for the fourth-row main-group elements are constructed in a manner analogous to previous developments of first-,[15a] second-,[15b] and third-row[15c] (main group) representations. Basis sets for rubidium and strontium comprise 22 atomic orbitals:

1s
2s, $2p_x$, $2p_y$, $2p_z$
3s, $3p_x$, $3p_y$, $3p_z$, $3d_{3z^2-r^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$
4s, $4p_x$, $4p_y$, $4p_z$
5s, $5p_x$, $5p_y$, $5p_z$

Descriptions for the remainder of the main-group elements are in terms of 27 orbitals:

1s
2s, $2p_x$, $2p_y$, $2p_z$
3s, $3p_x$, $3p_y$, $3p_z$, $3d_{3z^2-r^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$
4s, $4p_x$, $4p_y$, $4p_z$, $4d_{3z^2-r^2}$, $4d_{x^2-y^2}$, $4d_{xy}$, $4d_{xz}$, $4d_{yz}$
5s, $5p_x$, $5p_y$, $5p_z$

The sets of five pure d-type atomic orbitals used in these representations have been constructed as linear combinations of the full set of six second-order functions (i.e., x^2, y^2, z^2, xy, xz, yz). Note that the representations for rubidium and strontium are not strictly minimal, as they include 5p functions which are not occupied in the atomic ground state. Previous experience with basis sets for the corresponding earlier-row elements[15] suggests that the inclusion of low-lying but empty p-type functions is necessary for proper description of the bonding in most compounds.

Following past practices,[15] each Slater-type atomic orbital, ϕ, has been replaced by a linear combination of N Gaussian type functions, ϕ':

$$\phi_{ns}(1,\mathbf{r}) \rightarrow \phi'_{ns}(1,\mathbf{r}) = \sum_{k=1}^{N} d_{ns,k} g_{1s}(\alpha_{nk},\mathbf{r}) \qquad n = 1\text{–}5$$

$$\phi_{np}(1,\mathbf{r}) \rightarrow \phi'_{np}(1,\mathbf{r}) = \sum_{k=1}^{N} d_{np,k} g_{2p}(\alpha_{nk},\mathbf{r}) \qquad n = 2\text{–}5$$

$$\phi_{nd}(1,\mathbf{r}) \rightarrow \phi'_{nd}(1,\mathbf{r}) = \sum_{k=1}^{N} d_{nd,k} g_{3d}(\alpha_{nk},\mathbf{r}) \qquad n = 3,4$$

where g_{1s}, g_{2p}, and g_{3d} are normalized Gaussians. The Gaussian exponents, α, and the expansion coefficients, d, have been chosen by least squares as best fits to Slater orbitals of exponent $\zeta = 1$. The same set of Gaussian exponents, α_{nk}, are common to all fits of given n quantum number, a restriction which leads to significant gains in the computational efficiency of integral evaluation. Least-squares fits to ϕ_{1s}, ϕ_{2s}, ϕ_{2p}, ϕ_{3s}, ϕ_{3p}, and ϕ_{3d} have been presented earlier for expansions comprising between two and six Gaussians.[15] Fits to ϕ_{4s} and ϕ_{4p} have also been obtained previously for use in STO-3G basis sets for third-row elements.[15c] These are, however, inappropriate for our present use with fourth-row elements as they have been constructed without consideration of the corresponding 4d-type functions. New expansions fit simultaneously by least squares to Slater-type 4s, 4p, and 4d functions are presented in Table I for values of N between 2 and 6. Also included are the best simultaneous fits to ϕ_{5s} and ϕ_{5p}. Only the three-Gaussian fit will be discussed in the context of the present work. The remaining expansions are included for the sake of completeness.

Least-squares fits to orbitals of arbitrary exponent may be obtained by scaling[15a]

$$\phi(\zeta,\mathbf{r}) = \zeta^{3/2}\phi(1,\zeta\mathbf{r})$$

the same factors (exponents) being used for all atomic orbitals of given n quantum number (i.e., $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$, $\zeta_{4s} = \zeta_{4p} = \zeta_{4d}$, and $\zeta_{5s} = \zeta_{5p}$). Previous experience with lighter elements suggests that these exponent restrictions, which enable significant gains in the efficiency of integral evaluation, detract little from the quality of the basis set.

Standard single-determinant molecular orbital theory has been employed throughout.[16] Open-shell systems have been treated with the use of the unrestricted Hartree–Fock procedure of Pople and Nesbet.[17] No attempt has been made to account for relativistic effects. All calculations have been

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Table I. Coefficients and Exponents for Constrained Gaussian Expansions (4s = 4p = 4d and 5s = 5p) of Slater-Type Orbitals

expansion length, N	α_4	d_{4s}	d_{4p}	d_{4d}	α_5	d_{5s}	d_{5p}
2	1.26011 (−1)	−6.56197 (−1)	1.27008 (−1)	5.43275 (−1)	8.12432 (−2)	−1.09369	−1.04740 (−1)
	5.00901 (−2)	1.50354	8.98533 (−1)	5.42087 (−1)	3.93036 (−2)	1.88137	1.08763
3	2.33486 (−1)	−3.30610 (−1)	−1.28393 (−1)	1.25066 (−1)	1.34901 (−1)	−3.84264 (−1)	−3.48169 (−1)
	9.09182 (−2)	5.76110 (−2)	5.85205 (−1)	6.68679 (−1)	7.26361 (−2)	−1.97257 (−1)	6.29032 (−1)
	4.00224 (−2)	1.11558	5.43944 (−1)	3.05247 (−1)	3.20846 (−2)	1.37550	6.66283 (−1)
4	4.50425 (−1)	−5.84688 (−2)	−6.74634 (−2)	3.86994 (−3)	2.57771 (−1)	4.04511 (−2)	−8.58615 (−2)
	1.60793 (−1)	−4.39804 (−1)	2.07793 (−2)	2.97612 (−1)	1.18964 (−1)	−6.57669 (−1)	−1.09015 (−1)
	7.16348 (−2)	5.31922 (−1)	6.88454 (−1)	6.20373 (−1)	5.27078 (−2)	3.79252 (−1)	7.23404 (−1)
	3.51148 (−2)	8.10747 (−1)	3.51482 (−1)	1.73553 (−1)	2.87036 (−2)	1.03859	4.11743 (−1)
5	8.14733 (−1)	−1.62523 (−3)	−2.25272 (−2)	−7.36629 (−3)	4.82262 (−1)	3.03766 (−2)	−1.25767 (−2)
	2.73043 (−1)	−2.02142 (−1)	−8.33081 (−2)	6.95976 (−2)	1.81352 (−1)	−1.82506 (−1)	−1.56394 (−1)
	1.19670 (−1)	−3.15702 (−1)	2.02471 (−1)	4.23805 (−1)	8.58891 (−2)	−6.59149 (−1)	6.50075 (−2)
	5.98104 (−2)	8.08210 (−1)	6.76431 (−1)	5.07395 (−1)	4.61741 (−2)	9.18693 (−1)	7.85982 (−1)
	3.14652 (−2)	5.57217 (−1)	2.18597 (−1)	1.00361 (−1)	2.58255 (−2)	6.95274 (−1)	2.58228 (−1)
6	1.37434	3.71377 (−3)	−6.87731 (−3)	−4.34638 (−3)	7.70142 (−1)	1.26745 (−2)	−1.10568 (−3)
	4.46516 (−1)	−5.21220 (−2)	−5.08511 (−2)	4.89123 (−3)	2.34839 (−2)	4.36850 (−1)	1.49315 (−1)
	1.92451 (−1)	−3.07763 (−1)	−4.20645 (−2)	1.63480 (−1)	4.00255 (−2)	1.10432	6.96458 (−1)
	9.58282 (−2)	−6.45125 (−2)	3.65240 (−1)	4.80748 (−1)	6.95344 (−2)	−3.23200 (−1)	3.21033 (−1)
	5.16642 (−2)	8.98078 (−1)	5.91591 (−1)	3.90692 (−1)	1.30185 (−1)	−4.30756 (−1)	−1.62848 (−1)
	2.85894 (−2)	3.69096 (−1)	1.34413 (−1)	5.78663 (−2)	2.75627 (−1)	3.26670 (−3)	−6.24314 (−2)

Table II. Optimum Exponents and Ground-State (UHF) Energies for Fourth-Row Main-Group Elements (STO-3G Basis Sets)

	optimum exponent					
atom (state)	ζ_{1s}	$\zeta_{2s} = \zeta_{2p}$	$\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$	$\zeta_{4s} = \zeta_{4p} = \zeta_{4d}$	$\zeta_{5s} = \zeta_{5p}$	E, hartrees
Rb (^{2}S)	36.32	15.81	7.18	3.02[a]	1.64	−2907.637 56
Sr (^{1}S)	37.31	16.28	7.49	3.16[a]	1.47	−3099.182 82
In (^{2}P)	48.12	21.33	11.08	4.65	1.74	−5682.849 84
Sn (^{3}P)	49.10	21.79	11.39	4.89	1.91	−5963.270 64
Sb (^{4}S)	50.08	22.25	11.71	5.12	2.09	−6251.381 89
Te (^{3}P)	51.07	22.71	12.03	5.36	2.25	−6457.124 45
I (^{2}P)	52.05	23.17	12.35	5.59	2.41	−6850.676 53
Xe (^{1}S)	53.03	23.63	12.66	5.82	2.57	−7162.104 64

[a] $\zeta_{4s} = \zeta_{4p}$ only.

carried out with the use of Gaussian 77 series of programs[18] on a Harris Corp. Slash 6 minicomputer.

Results and Discussion

Optimum scale factors for atoms (in their electronic ground states), determined at the STO-3G level, are presented in Table II. Values for ζ_{1s} differ only slightly from the optimized minimal basis set STO descriptions of Clementi, Raimondi, and Reinhardt.[19] Due to exponent constraints within a given n quantum number, the remaining scale factors differ significantly from the previously obtained and unconstrained STO values. STO-3G atom energies based on these optimum scale factors are also given in Table II. They are consistently 0.8% higher than the "best ζ" values given in ref 19, precisely the same fraction as noted in earlier work on third-row elements.[15c]

Paralleling previous work, inner-shell exponents (ζ_{1s}, $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$, $\zeta_{4s} = \zeta_{4p} = \zeta_{4d}$) have been fixed at their respective best atom values, and an "average" valence-shell scale factor ($\zeta_{5s} = \zeta_{5p}$), suitble for use in calculations on molecules, has been selected for each atom. The selection itself is based on the optimization of the valence-shell scale factors in a small number of molecules for each element. These values, given in Table III, have been obtained with the assumptions of experimental equilibrium geometries and standard scale factors for all other (non-fourth-row) elements involved. The proposed set of standard valence-shell scale factors for the fourth-row main-group elements chosen as representative of the molecules considered is found in Table IV. The value for xenon is that value appropriate for the free atom. These standard scale factors are employed in all molecular calculations which follow.

Table III. Optimum 5s, 5p Scale Factors for Molecules Containing Fourth-Row Main-Group Elements[a]

atom	molecule	$\zeta_{5s} = \zeta_{5p}$	atom	molecule	$\zeta_{5s} = \zeta_{5p}$
Rb	RbH	1.76	Sn	SnH_4	2.04
	RbF	1.91		$Sn(CH_3)_4$	2.18
	RbOH	1.98		$SnCl_4$	2.40
	RbBr	1.99	Sb	SbH_3	2.17
	RbCl	2.05		$Sb(CH_3)_3$[e]	2.19
Sr	SrO[f]	1.52		$SbCl_3$	2.28
	SrF_2[b]	1.85	Te	S=C=Te	2.26
	$SrCl_2$[b]	1.93		TeH_2	2.29
In	$In(CH_3)_3$[c]	2.04		$TeBr_2$	2.30
	InF_3[d]	2.06	I	CH_3I	2.42
				HI	2.43
				I_2	2.43

[a] Calculations were performed with the assumption of experimental equilibrium geometries. Unless otherwise noted, data on polyatomic molecules are from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pole, "Structure Data on Free Polyatomic Molecules", Landolt-Bornstein, New Series, Group II, Vol. 7, K. H. Hellwege and A. M. Hellwege, Eds., Springer-Verlag, Berlin, 1976. Data on diatomic molecules from Vol. 6 of this series. [b] P. A. Arishin and V. P. Spiridonov, *Kristallografiya*, 2, 475 (1957). [c] G. Barbe, J. L. Hencher, Q. Shen, and D. G. Tuck, *Can. J. Chem.*, 52, 3936 (1974). [d] Geometry of $INF_3 \cdot 3H_2O$ employed: G. B. Bokii and T. S. Khodashova, *Kristallografiya*, 1, 197 (1956). [e] Geometry of $Sb(CF_3)_3$ employed, assuming r(CH) = 1.09 Å: H. J. M. Bowen, *Trans. Faraday Soc.*, 50, 463 (1954). [f] M. Kaufman, L. Wharton, and W. Klemperer, *J. Phys. Chem.*, 43, 943 (1965).

Table IV. Standard Valence-Shell Factors for Fourth-Row Main-Group Elements (STO-3G Basis Set)

atom	$\zeta_{5s} = \zeta_{5p}$	atom	$\zeta_{5s} = \zeta_{5p}$
Rb	1.90	Sb	2.20
Sr	1.80	Te	2.28
In	2.05	I	2.42
Sn	2.15	Xe	2.57

Specification of the STO-3G basis set for fourth-row main-group elements is now complete. A comparison of theoretical STO-3G and experimental equilibrium structures

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Table V. STO-3G and Experimental Equilibrium Geometries of Molecules Containing Fourth-Row Main-Group Elements (Bond Lengths in Å, Angles in Degrees)

molecule	point group	geometric parameter	STO-3G	exptl[a]
RbH	$C_{\infty v}$	r(RbH)	2.211	2.367
SnH_4	T_d	r(SnH)	1.630	1.711
SbH_3	C_{3v}	r(SbH)	1.644	1.704
		∠(HSbH)	94.4	91.6
TeH_2	C_{2v}	r(TeH)	1.624	1.658
		∠(HTeH)	92.4	90.3
HI	$C_{\infty v}$	r(HI)	1.599	1.609
RbOH	$C_{\infty v}$	r(RbO)	2.308	2.301
		r(OH)	1.000	0.957
RbF	$C_{\infty v}$	r(RbF)	2.365	2.270
RbCl	$C_{\infty v}$	r(RbCl)	2.810	2.787
RbBr	$C_{\infty v}$	r(RbBr)	2.920	2.945
RbI	$C_{\infty v}$	r(RbI)	3.170	3.177
SrO[d]	$C_{\infty v}$	r(SrO)	2.584	1.920[d]
SrF_2[b]	$D_{\infty h}$	r(SrF)	2.321	2.20
$SrCl_2$[b]	$D_{\infty h}$	r(SrCl)	2.701	2.67
$SrBr_2$[b]	$D_{\infty h}$	r(SrBr)	2.832	2.82
SrI_2[b]	$D_{\infty h}$	r(SrI)	3.059	3.03
$In(CH_3)_3$[c,e]	C_{3h}	r(InC)	2.090	2.093
		$r(CH_a)$	1.082	1.140[g]
		$r(CH_b)$	1.084	1.140[g]
		$\angle(InCH_a)$	113.4	
		$\angle(InCH_{bb})$[f]	128.6	
		$\angle(H_bCH_b)$	105.9	106.1[h]
InC_5H_5	C_{5v}	r(InC)	2.420	2.621
		r(CC)	1.414	1.427
		r(CH)	1.080	1.10
		∠(α)[i]	0.6	4.5
$Sn(CH_3)_4$	T_d	r(SnC)	2.110	2.144
		r(CH)	1.082	1.118
		∠(HCH)	107.0	106.8
SnO	$C_{\infty v}$	r(SnO)	1.712	1.833
$SnCl_4$	T_d	r(SnCl)	2.293	2.281
SnH_3Br	C_{3v}	r(SnBr)	2.460	2.469
		r(SnH)	1.630	1.767
		∠(HSnH)	111.7	112.8
$SbCl_3$	C_{3v}	r(SbCl)	2.352	2.333
		∠(ClSbCl)	94.9	97.2
$SbBr_3$	C_{3v}	r(SbBr)	2.490	2.490
		∠(BrSbBr)	98.2	98.2
Te=C=S	$C_{\infty v}$	r(TeC)	1.859	1.904
		r(CS)	1.517	1.557
$TeBr_2$	C_{2v}	r(TeBr)	2.512	2.51
		∠(BrTeBr)	98.0	98.0
LiI	$C_{\infty v}$	r(LiI)	2.281	2.392
CH_3I	C_{3v}	r(CI)	2.110	2.132
		r(CH)	1.084	1.084
		∠(HCH)	108.9	111.2
ICN	$C_{\infty v}$	r(CI)	1.991	1.995
		r(CN)	1.157	1.159
IF	$C_{\infty v}$	r(IF)	1.962	1.908
NaI	$C_{\infty v}$	r(NaI)	2.561	2.711
SiH_3I	C_{3v}	r(SiI)	2.438	2.437
		r(SiH)	1.423	1.457
		∠(HSiH)	109.9	110.5
ICl	$C_{\infty v}$	r(ICl)	2.367	2.321
KI	$C_{\infty v}$	r(KI)	3.014	3.048
IBr	$C_{\infty v}$	r(IBr)	2.497	2.485
I_2	$D_{\infty h}$	r(II)	2.703	2.667

[a] See footnote *a* of Table III for reference to experimental structure data. [b] See footnote *b* of Table III for reference to experimental structure data. [c] See footnote *c* of Table III for reference to experimental structure data. [d] See footnote *f* of Table III for reference to experimental structure data. [e] Hydrogens subscripted a are in the plane containing the three carbons and the indium. Hydrogens subscripted b refer to the out-of-plane hydrogens. [f] Defined as the angle between the (H_bCH_b) bisector and the line formed by (InC). [g] Assumed equal. [h] All (HCH) angles assumed equal. [i] Defined as the angle (exo) between the hydrogens and the plane of the ring.

Table VI. Total Atomic and Molecular Energies (hartrees)

atom or molecule	STO-3G	atom or molecule	STO-3G
Rb	−2907.604 27	SrI_2	−16800.704 66
Sr	−3099.116 73	$In(CH_3)_3$	−5800.366 81
In	−5682.777 39	InC_5H_5	−5872.774 86
Sn	−5963.206 13	$Sn(CH_3)_4$	−6119.988 52
Sb	−6251.362 46	SnO	−6037.055 98
Te	−6547.122 36	$SnCl_4$	−7781.917 84
I	−6850.676 25	SnH_3Br	−8509.778 26
Xe	−7162.104 21	$SbCl_3$	−7615.257 20
RbH	−2908.127 41	$SbBr_3$	−13885.508 68
SnH_4	−5965.618 84	Te=C=S	−6977.676 73
SbH_3	−6253.083 46	$TeBr_2$	−11636.515 67
TeH_2	−6548.267 82	LiI	−6858.120 90
HI	−6851.254 27	CH_3I	−6889.840 14
RbOH	−2981.973 50	ICN	−6941.805 04
RbF	−3005.609 07	IF	−6948.666 34
RbCl	−3362.339 46	NaI	−7010.628 86
RbBr	−5452.400 88	SiH_3I	−7138.081 87
RbI	−9758.450 50	ICl	−7305.269 98
SrO	−3172.802 86	KI	−7443.857 79
SrF_2	−3295.100 53	IBr	−9395.366 56
$SrCl_2$	−4008.488 07	I_2	−13701.405 65
$SrBr_2$	−8188.624 36		

for a number of simple polyatomic molecules containing one or more fourth-row elements is presented in Table V. The set of total energies corresponding to these optimum structures is presented in Table VI. Molecules with expanded valence shells have been excluded from the present comparison. Previous experience with second-row elements suggests that the STO-3G basis set performs poorly with regard to the calculation of the structures of hypervalent compounds, and furthermore that the addition of diffuse d-type functions to the basis set leads to significant improvements in the calculated geometries of such compounds.[20] Investigation of the possible effects of such additions to the STO-3G minimal basis sets for third- and fourth-row main-group elements will be the subject of future research.

Equilibrium bond lengths in the simple one heavy-atom hydrides are consistently shorter than the corresponding experimental values. The deviation between theory and experiment is greatest for RbH (0.156 Å) and diminishes as one proceeds across the row to SnH_4 (0.081 Å), SbH_3 (0.060 Å), TeH_2 (0.032 Å), and HI (0.010 Å). This same trend is also observed in the comparison of STO-3G and experimental equilibrium bond distances for the corresponding earlier row hydrides. In fact, as is displayed in Figure 1, a rough linear correlation exists between the signed deviation of the calculated bond length from experiment and the Pauling electronegativity of the heavy atom. Here it can be seen that bonds to elements less electronegative or only slightly more electronegative than hydrogen are calculated to be too short, while linkages to atoms of significantly greater electronegativity are longer than the corresponding experimental values. Experience with more extensive basis set calculations on the lighter hydrides suggests that the errors noted here are due in great part to the inability of the minimal STO-3G basis set to properly describe the bonding in highly polar molecules, rather than any basic defficiency in the single determinant Hartree–Fock model. That is to say, calculations on first- and second-row hydrides using split-valence or larger atomic orbital representations which are capable of adequately describing highly anisotropic molecular environments lead to bond lengths which are in far better agreement with the experimental data.

Calculated equilibrium bond angles in SbH_3 and TeH_2 are in close agreement with their respective experimental values.

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(20) J. B. Collins, P. V. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

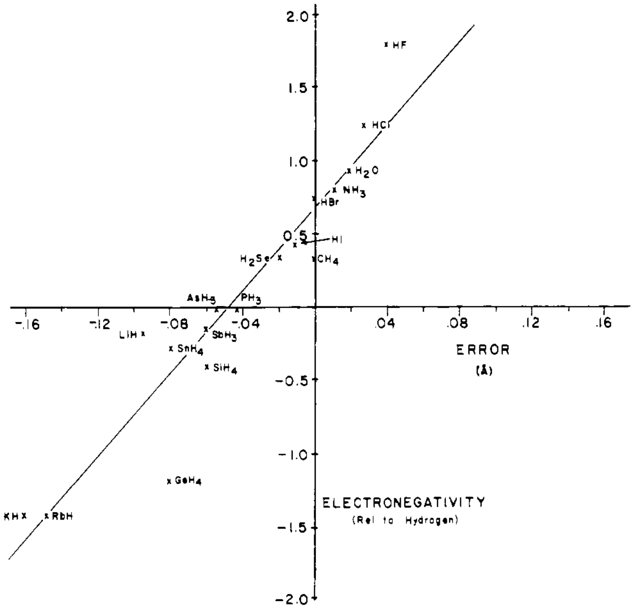

Figure 1. Bond length errors of simple hydrides.

Single bonds involving two heavy atoms (at least one of which is a fourth-row element) are generally well described by the minimal basis set STO-3G calculations. The worst cases are the highly polar species RbF, SrF_2, LiI, and NaI, although RbBr and RbI are described unexpectedly well. The calculated bond lengths in RbF and SrF_2, which involve a highly electropositive fourth-row element and the highly electronegative fluorine atom, are longer than their respective experimental values (by 0.095 and 0.12 Å), while calculated bond distances for LiI and NaI, in which a highly electropositive lithium or sodium atom is bound to the relatively electronegative iodine atom, are shorter than experimental values (by 0.111 and 0.150 Å, respectively). Again we suspect that the inherent inflexibility of the minimal representation precludes its adequate description of the bonding in these highly anisotropic species.

The largest deviations from experiment in calculated heavy-atom bond lengths for the remaining molecules dealt with are on the order of 0.01–0.03 Å, the same range of values typically found in dealing with STO-3G calculations involving lighter elements.[15] Of particular importance to the future role of the theory in describing the properties of main-group organometallic compounds is the fact that bonds to carbon are particularly well described. Due to a scarcity of gas-phase experimental structural data, comparisons between calculated and measured bond distances for linkages involving either nitrogen or oxygen (or their second- or third-row analogues) are unavailable. However, numerous examples of bonds between a fourth-row element and a halogen exist. Here, calculated bond lengths are generally in very good accord with the experimental data.

The equilibrium structures of only a very few simple compounds incorporating a multiple bond to a fourth-row element have been determined experimentally. In two of the three cases considered (SrO and SnO), the theory performs very poorly, yielding equilibrium bond lengths which are too long by 0.664 Å and too short by 0.121 Å, respectively. The calculated TeC bond distance in Te=C=S is also shorter than the experimental value, but only by 0.046 Å. The overall poor performance with regard to the calculation of the lengths of multiple bonds here is to have been expected, in view of previous experience with such linkages involving first-, second-, and third-row atoms. The usual explanation for the failure, that the high anisotropy of the valence electron distribution in such systems cannot be properly accounted for by an isotopic minimal basis set, suggests that split-valence and higher-level atomic orbital representations will fare much better. Work in this direction is in progress.

The calculated equilibrium structure of the half-sandwich compound cyclopentadenylindium is not in very good accord with the experimental geometry, at least as far as the metal–ring separation is concerned. Whether the shortcoming of the theory is due to the highly polar nature of the compound (i.e., $In^+C_5H_5^-$) or to the inadequacy of the Hartree–Fock basis set (i.e., the need for inclusion of low-lying but unfilled 5d functions) is unclear to us at the present time.

Conclusion

The STO-3G minimal basis set has already found extensive use as a tool for the elucidation of structure of simple organic molecules. It represents perhaps the simplest level of nonempirical theory which has met with wide success in this respect. The results here, together with those earlier presented for third-row main-group elements, strongly suggest that the STO-3G method is also moderately successful in accounting for the equilibrium geometrical structures of molecules comprising heavy elements.

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Registry No. Rb, 7440-17-7; Sr, 7440-24-6; In, 7440-74-6; Sn, 7440-31-5; Sb, 7440-36-0; Te, 13494-80-9; I, 14362-44-8; Xe, 7440-63-3.