From the values of the force constant for the Jahn–Teller active vibrations, we compute vibrational energies of 147 (calculated) and 91 (observed) cm^{-1} and zero-point amplitudes of 0.34 and 0.44 Å, respectively, the latter values indicating that the Jahn–Teller distortion in Cu(pyO)$_6^{2+}$ is essentially static in the radial coordinate. However, we find reasonably large zero-point motion in the coordinate θ, assuming that the angular potential can also be treated with a simple harmonic approximation. A value of 16° is obtained for the root-mean-square angular displacement from the set of parameters E_{JT}, R_{JT}, and B.

For appreciable zero-point motion O'Brien[39] has shown that the threefold degeneracy of the ground-state minima is removed and the **g** tensor behavior for the three sites modified. For the Jahn–Teller parameters derived from the Hückel calculation we find that the overlap between the ground-state angular functions in neighboring wells is relatively small and that it yields a value of 0.036 cm^{-1} for the separation of the ground-state doublet and the first excited singlet (3Γ), assuming the calculated barrier height of 72 cm^{-1}. This splitting is comparable to the **g** anisotropy $(g_\parallel - g_\perp)\beta H$ of 0.038 cm^{-1} for X-band frequency. For localized or static sites to be observed at low temperatures, $\Delta g\beta H$ should, however, be greater than 3Γ. A comparable value for 3Γ is obtained from the experimental values of the Jahn–Teller parameters.

Although a barrier height in the region of 50 cm^{-1} is just consistent with the formation of an anisotropic three-site spectrum at low temperatures, this value is a lower limit. As suggested earlier, random strain is then almost certainly a significant factor in producing the statically distorted sites in this system. The barrier tunneling rate in the lowest vibrational state, calculated according to the formula given by Sturge,[16] supports this picture, for the approximate value of 1.25 × 10^{10} s^{-1} is in fact appreciably larger than the frequency differences between the three sites.

The **g** and hyperfine tensors were calculated according to the formulas given previously.[52] The elements of the copper atom anisotropic hyperfine tensor were calculated in first order, and contributions from ligand atoms were neglected. The **g** and A values given in Table V are those for the elongated minimum. The calculated orientations of both the **g** and **A** tensors were found to deviate very little from the molecular axes—taken to be coincident with the M–O bond directions—despite the fact that the complex cation has only $\bar{1}$ symmetry. This is in contrast with the experimental results which, especially for the **A** tensor, show significant deviations from the tetragonal axes.

Contribution from the Departments of Chemistry, University of California, Irvine, California 92717, and Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Molecular Orbital Theory of the Properties of Inorganic and Organometallic Compounds. 1. STO-*N*G Basis Sets for Third-Row Main-Group Elements

WILLIAM J. PIETRO,[1a] BEVERLY A. LEVI,[1a] WARREN J. HEHRE,*[1a] and ROBERT F. STEWART[1b]

An STO-3G basis set has been proposed for the main-group elements of the third row. Equilibrium geometries calculated by using this minimal representation are generally in close accord with available experimental data. The related smaller STO-2G basis set does not perform equally well in the task of structure calculation.

Introduction

The STO-3G minimal basis set[2] has been widely employed for ab initio molecular orbital calculations on polyatomic molecules containing first- and second-row elements. It has met with considerable success in several areas of application, perhaps most dramatically with regard to the calculation of molecular equilibrium geometries. Because of its small size and relatively efficient construction, complete structure optimizations on molecules of moderate size (10–15 atoms) have now become routine. Literally hundreds of theoretical STO-3G equilibrium geometries have appeared in the literature,[3] and the dozens of critical comparisons which have been made with experimentally determined structures indicate an overall high level of performance of the theoretical method.

In this paper we extend the STO-3G basis set to the main-group elements of the third row. Later papers in this series will consider applications to first-row transition metals. We have selected the main-group elements over the metals as a starting point for two principal reasons. For one, there exist a fair amount of gas-phase structural data on molecules containing third-row main-group elements; very little gas-phase data is available for metallic systems. A far more complete assessment of the performance of STO-3G in the former area

---

(1) (a) University of California. (b) Carnegie-Mellon University.
(2) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).

(3) Compilations include: (a) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974); (b) J. A. Pople, *Mod. Theor. Chem.*, **4**, 1 (1977).

Table I. Coefficients and Exponents for Constrained Gaussian Expansions of Slater-Type Orbitals[a]

expansion length, N	α_3	d_{3s}	d_{3p}	d_{3d}	α_4	d_{4s}	d_{4p}
2	2.236 02 (−1)	−3.121 72 (−1)	2.940 03 (−1)	6.006 04 (−1)	1.242 35 (−1)	−6.615 60 (−1)	1.309 89 (−1)
	6.915 73 (−2)	1.225 40	7.800 42 (−1)	5.292 04 (−1)	4.999 75 (−2)	1.510 75	8.946 43 (−1)
3	4.559 50 (−1)	−2.277 64 (−1)	4.951 51 (−3)	2.197 68 (−1)	2.464 58 (−1)	−3.088 44 (−1)	−1.215 47 (−1)
	1.390 79 (−1)	2.175 44 (−1)	5.777 66 (−1)	6.555 47 (−1)	9.095 86 (−2)	1.960 64 (−2)	5.715 23 (−1)
	5.366 12 (−2)	9.166 77 (−1)	4.846 46 (−1)	2.865 73 (−1)	4.016 83 (−2)	1.131 03	5.498 95 (−1)
4	8.642 19 (−1)	−8.888 86 (−2)	−2.580 36 (−2)	6.920 77 (−2)	4.389 53 (−1)	−5.893 56 (−2)	−7.180 52 (−2)
	2.587 58 (−1)	−2.026 19 (−1)	1.591 41 (−1)	3.728 16 (−1)	1.624 45 (−1)	−4.289 23 (−1)	3.726 86 (−2)
	1.026 34 (−1)	5.450 89 (−1)	6.284 12 (−1)	5.664 09 (−1)	6.983 98 (−2)	5.473 00 (−1)	6.965 84 (−1)
	4.562 80 (−2)	6.517 02 (−1)	3.009 84 (−1)	1.585 95 (−1)	3.469 20 (−2)	7.853 69 (−1)	3.310 24 (−1)
5	1.560 01	−2.996 08 (−2)	−1.665 12 (−2)	2.129 97 (−2)	7.857 76 (−1)	−1.628 25 (−3)	−2.399 52 (−2)
	4.589 58 (−1)	−1.549 05 (−1)	9.090 22 (−3)	1.576 72 (−1)	2.685 95 (−1)	−2.138 93 (−1)	−8.118 32 (−2)
	1.818 19 (−1)	−5.893 27 (−2)	2.985 63 (−1)	4.485 17 (−1)	1.155 68 (−1)	−3.039 58 (−1)	2.238 63 (−1)
	8.295 17 (−2)	7.044 19 (−1)	5.832 01 (−1)	4.495 37 (−1)	5.839 87 (−2)	8.491 18 (−1)	6.726 90 (−1)
	4.009 49 (−2)	4.445 30 (−1)	1.867 09 (−1)	9.122 49 (−2)	3.082 65 (−2)	5.164 15 (−1)	2.003 80 (−1)
6	2.730 51	−9.737 40 (−3)	−8.104 94 (−3)	6.633 43 (−3)	1.365 35	3.775 06 (−3)	−7.052 08 (−3)
	7.862 47 (−1)	−7.265 88 (−2)	−1.715 48 (−2)	5.958 18 (−2)	4.393 21 (−1)	−5.585 97 (−2)	−5.259 51 (−2)
	3.092 51 (−1)	−1.716 16 (−1)	7.369 79 (−2)	2.401 95 (−1)	1.877 07 (−1)	−3.192 95 (−1)	−3.773 45 (−2)
	1.413 38 (−1)	1.289 78 (−1)	3.965 15 (−1)	4.648 11 (−1)	9.360 27 (−2)	−2.764 78 (−2)	3.874 77 (−1)
	7.033 91 (−2)	7.288 61 (−1)	4.978 08 (−1)	3.434 09 (−1)	5.052 26 (−2)	9.049 20 (−1)	5.791 67 (−1)
	3.612 35 (−2)	3.013 32 (−1)	1.174 83 (−1)	5.389 06 (−2)	2.809 35 (−2)	3.406 26 (−1)	1.221 82 (−1)

is therefore possible. Secondly, calculations involving the main-group elements, unlike those involving transition metals, are for the most part uncomplicated by the presence of low-lying excited electronic states. This should be of aid in isolating those failings of the theory which result from deficiencies in the basis set from problems associated with the restriction of single-determinant wave functions.

Very little previous theoretical work exists on molecules containing third-row main-group elements.[4] Somewhat more attention has been given to studies involving the first-row transition metals.[5] Even less effort has been expended on the determination of equilibrium structures of these compounds; most theoretical studies reported thus far utilize assumed or experimental geometries. The only previous theoretical studies of direct relevance to our present efforts are those of Stevenson and Lipscomb[4b] and of Dixon and Marynick[4m] both of which employed a minimum basis set of Slater-type orbitals. The latter authors report a theoretical equilibrium geometry for AsH₃ (r(AsH) = 1.528 Å, ∠(HAsH) = 93.6°) which is in good accord with the experimental structure (r(AsH) = 1.511 Å, ∠(HAsH) = 92.1°).

Methods

STO-3G minimal basis sets for the main-group elements of the third row are constructed in a manner analogous to previous developments of first- and second-row representations.[2] Basis sets for potassium and calcium comprise 13 atomic orbitals:

1s
2s, 2p$_x$, 2p$_y$, 2p$_z$
3s, 3p$_x$, 3p$_y$, 3p$_z$
4s, 4p$_x$, 4p$_y$, 4p$_z$

(4) (a) K. D. Carlson, K. Kaiser, C. Moser, and A. C. Wahl, *J. Chem. Phys.*, **52**, 4678 (1970); (b) P. E. Stevenson and W. N. Lipscomb, *ibid.*, **52**, 5343 (1970); (c) R. L. Matcha, *ibid.*, **53**, 485 (1970); (d) R. L. Matcha, *ibid.*, **53**, 4490 (1970); (e) B. Liu and H. F. Schaefer, *ibid.*, **55**, 2369 (1971); (f) J. Berkowitz and J. L. Dehmer, *ibid.*, **57**, 3194 (1972); (g) J. L. Gole, A. K. Q. Sin, and E. F. Hayes, *ibid.*, **58**, 857 (1973); (h) H. Kistenmacher, H. Popkie, and E. Clementi, *ibid.*, **58**, 1689 (1973); (i) H. Kistenmacher, J. Popkie, and E. Clementi, *ibid.*, **59**, 5842 (1973); (j) P. A. G. O'Hare, A. Batana, and A. C. Wahl, *ibid.*, **59**, 6495 (1973); (k) C. S. Ewig and J. R. van Wazer, *ibid.*, **65**, 2035 (1976); (1976); (l) J. N. Murrell and C. E. Scollary, *J. Chem. Soc., Dalton Trans.*, 818 (1976); (m) D. A. Dixon and D. S. Marynick, *J. Am. Chem. Soc.*, **99**, 6101 (1977); (n) J. Prissette, G. Seger, and E. Kochanski, *ibid.*, **100**, 6941 (1978).

(5) For a recent review see: A. Veillard and J. Demuynck, *Mod. Theor. Chem.*, **4**, 187 (1977).

Descriptions for the remainder of the main-group elements are in terms of 18 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$_z$

The five d-type atomic orbitals 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). While the representations for potassium and calcium are not strictly minimal (i.e., they include 4p functions which are not occupied in the atomic ground state), previous experience with basis sets for the corresponding first- and second-row elements suggests that the inclusion of low-lying but empty p-type functions is necessary for proper description of the bonding in most compounds containing these elements.

Following past practices,[2] each Slater-type atomic orbital, φ, is replaced by a linear combination of N Gaussian-type functions, φ':

$$\varphi_{ns}(1,\mathbf{r}) \rightarrow \varphi'_{ns}(1,\mathbf{r}) = \sum_{k=1}^{N} d_{ns,k} g_{1s}(\alpha_{nk},\mathbf{r}) \quad n = 1, 2, 3, 4$$

$$\varphi_{np}(1,\mathbf{r}) \rightarrow \varphi'_{np}(1,\mathbf{r}) = \sum_{k=1}^{N} d_{np,k} g_{2p}(\alpha_{nk},\mathbf{r}) \quad n = 2, 3, 4$$

$$\varphi_{nd}(1,\mathbf{r}) \rightarrow \varphi'_{nd}(1,\mathbf{r}) = \sum_{k=1}^{N} d_{nd,k} g_{3d}(\alpha_{nk},\mathbf{r}) \quad n = 3$$

Here 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 $\zeta = 1$. As indicated above, the same set of Gaussian exponents, α_{nk}, are common to all fits of given n quantum number. This restriction leads to significant gains in the computational efficiency of integral evaluation. Details have been presented elsewhere.[6] Least-squares fits to φ_{1s}, φ_{2s}, and φ_{2p} have been presented earlier for expansion lengths, n, of 2 through 6.[2a] Fits to φ_{3s} and φ_{3p} have also been published.[2b] These are, however, inappropriate for use in the present work as they were developed without explicit consideration of φ_{3d}. New least-squares fits simultaneously to 3s, 3p, and 3d type Slater orbitals have now been obtained and are presented in

(6) J. A. Pople and W. J. Hehre, *J. Comput. Phys.*, **27**, 161 (1978).

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

atom (state)	ζ_{1s}	$\zeta_{2s} = \zeta_{2p}$	$\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$	$\zeta_{4s} = \zeta_{4p}$	E, hartrees
K (^{2}S)	18.61	7.26	2.75^a	1.26	-593.085 18
Ca (^{1}S)	19.58	7.74	3.01^a	1.23	-669.998 47
Ga (^{2}P)	30.42	12.99	5.26	1.68	-1900.743 10
Ge (^{3}P)	31.40	13.47	5.58	1.84	-2051.671 75
As (^{4}S)	32.39	13.94	5.90	2.02	-2209.282 00
Se (^{3}P)	33.37	14.40	6.22	2.19	-2373.529 04
Br (^{2}P)	34.36	14.87	6.54	2.37	-2544.637 23
Kr (^{1}S)	35.34	15.34	6.86	2.54	-2722.706 00

^{a} $\zeta_{3s} = \zeta_{3p}$ only.

Table I for expansion lengths of 2 through 6. Also presented are best simultaneous fits to 4s and 4p Slater orbitals. Only the two and three Gaussian fits will be discussed in the context of the present work; the remaining expansions have been included for the sake of completeness.

Least-squares fits to orbitals of arbitrary exponent may be obtained by scaling.

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

The same scale factors (exponents) are used for all atomic orbitals of given n quantum number. Thus, $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$ and $\zeta_{4s} = \zeta_{4p}$. Previous experience with first- and second-row STO-*N*G basis sets has suggested 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[7] has been employed throughout. Open-shell systems have been treated by using the unrestricted Hartree–Fock procedure of Pople and Nesbet.[8] All calculations have been carried out by using the Gaussian 77 series of programs[9] on a Harris Corp. Slash 6 minicomputer.

Results and Discussion

STO-3G Basis Sets. Optimum scale factors for atoms (in their electronic ground states) have been determined at the STO-3G level by using UHF wave functions. They are presented in Table II. Values for ζ_{1s} differ only slightly from the optimized minimal basis set STO descriptions of Clementi and Raimondi.[10] 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 of Clementi and Raimondi.[10]

Following our previous practice[2] with the first- and second-row STO-3G basis sets, inner-shell exponents (ζ_{1s}, $\zeta_{2s} = \zeta_{2p}$, $\zeta_{3s} = \zeta_{3p} = \zeta_{3d}$) have been fixed at their respective best atom values and an "average" valence-shell scale factor ($\zeta_{4s} = \zeta_{4p}$), suitable for use in calculations on molecules, has been selected for each atom on the basis of limited optimization studies. Optimum 4s and 4p valence-shell scale factors for a number of molecules containing third-row main-group elements are given in Table III. These have been obtained by assuming experimental equilibrium geometries, as well as standard scale factors for all other (non-third-row) elements involved. The proposed set of standard valence-shell scale

Table III. Optimum 4s and 4p Scale Factors for Molecules Containing Main-Group Third-Row Elements

atom	molecule	$\zeta_{4s} = \zeta_{4p}$	atom	molecule	$\zeta_{4s} = \zeta_{4p}$
K	KH	1.32	As	CH$_3$AsH$_2$	2.07
	KOH	1.54		AsH$_3$	2.10
	KF	1.58		AsF$_3$	2.21
Ca	CaH$_2$	1.27	Se	COSe	2.20
	CaF$_2$	1.55		CH$_3$SeH	2.22
Ga	GaH$_3$	1.77		H$_2$Se	2.23
	GaF$_3$	1.90	Br	CH$_3$Br	2.37
Ge	GeH$_4$	1.96		Br$_2$	2.38
	CH$_3$GeH$_3$	1.98			
	GeH$_3$F	2.03			

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

atom	$\zeta_{4s} = \zeta_{4p}$	atom	$\zeta_{4s} = \zeta_{4p}$
K	1.43	As	2.12
Ca	1.36	Se	2.22
Ga	1.80	Br	2.38
Ge	2.00	Kr	2.54

factors for the third-row main-group elements is found in Table IV. The value for krypton is that appropriate to the free atom. These standard scale factors are employed in all molecular calculations which follow.

Specification of the STO-3G basis set for third-row main-group elements is now complete. A comparison of theoretical STO-3G and experimental structures for a number of simple polyatomic molecules containing one or more third-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 the second row suggests that the STO-3G basis set performs poorly with regard to the calculation of the structures of hypervalent compounds[11] and furthermore that the addition of diffuse d-type functions leads to significant improvements in calculated geometries. Extension of these concepts to hypervalent compounds containing third-row elements will be the subject of future research.

Bond lengths involving hydrogen and a third-row element are generally underestimated by the theory, the worst case being the bond to potassium in KH (to short by 0.16 Å) and the best being HBr, the bond length which is in nearly perfect accord with the experimental value. Bonds between first- (or second-) and third-row atoms are generally well described at the STO-3G level, the only major exceptions being the lengths of linkages involving the strongly electropositive elements, lithium, potassium, and calcium. Bonds between carbon and germanium (in methylgermane and germyl cyanide) and fluorine and germanium (in fluorogermane) are shorter than the corresponding experimental values, by 0.035, 0.077, and 0.026 Å, respectively. The calculated germanium chlorine bond length in germyl chloride is 0.010 Å longer than the experimental quantity. Bonds involving carbon and selenium, (in methyl selenol) and carbon and bromine (in bromomethane) are also somewhat too short at the STO-3G level (by 0.028 and 0.015 Å, respectively). The calculated arsenic–fluorine bond length in arsenic trifluoride and bromine–fluorine bond length in BrF are in good accord with their respective experimental values. The theoretical SiBr bond length in bromosilane closely reproduces the experimental quantity. The table provides only a single example of a multiple bond involving a third-row element, that between carbon and selenium in carbonyl selenide; here the theory underestimates the measured distance (by 0.047 Å). Exper-

(7) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23** 69 (1951).
(8) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).
(9) D. J. DeFrees, B. A. Levi, S. K. Pollack, E. N. Blurock, and W. J. Hehre, to be submitted to Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(10) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

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

Table V. STO-3G and Experimental Equilibrium Geometries of Molecules Containing Third-Row Main-Group Elements

molecule	point group	geometric parameter	STO-3G	exptl[a]
KH	$C_{\infty v}$	r(KH)	2.081	2.24
GeH$_4$	T_d	r(GeH)	1.430	1.525
AsH$_3$	C_{3v}	r(AsH)	1.456	1.511
		$\angle$(HAsH)	93.9	92.1
SeH$_2$	C_{2v}	r(SeH)	1.439	1.460
		$\angle$(HSeH)	92.4	90.6
HBr[d]	$C_{\infty v}$	r(HBr)	1.414	1.415
KCN	$C_{\infty v}$	r(KC)	2.540	2.294
		r(CN)	1.157	1.16
KOH	$C_{\infty v}$	r(KO)	2.158	2.212
		r(OH)	0.988	0.912
CaF$_2$[d]	C_{2v}[b]	r(CaF)	2.209	2.1
		$\angle$(FCaF)	180.0	135.0
H$_3$GeCH$_3$	C_{3v}	r(GeC)	1.910	1.945
		r(GeH)	1.433	1.529
		r(CH)	1.082	1.083
		$\angle$(HGeH)	109.3	109.3
		$\angle$(HCH)	107.4	108.4
H$_3$GeCN	C_{2v}	r(GeC)	1.842	1.919
		r(CN)	1.154	1.155
		r(GeH)	1.435	1.529
			110.8	$\cdots$
H$_3$GeF	C_{3v}	r(GeF)	1.706	1.732
		r(GeH)	1.435	1.522
		$\angle$(HGeH)	110.8	113.0
H$_3$GeCl	C_{3v}	r(GeCl)	2.160	2.150
		r(GeH)	1.434	1.537
		$\angle$(HGeH)	112.1	111.0
H$_3$Ge-GeH$_3$	D_{3d}	r(GeGe)	2.358	2.403
		r(GeH)	1.428	1.541
		$\angle$(HGeH)	108.5	106.4
H$_3$GeBr	C_{3v}	r(GeBr)	2.280	2.297
		r(GeH)	1.433	1.535
		$\angle$(HGeH)	110.8	106.9
AsF$_3$	C_{3v}	r(AsF)	1.710	1.710
		$\angle$(FAsF)	92.8	96.0
H$_3$CSeH	C_s	r(CSe)	1.931	1.959
		r(CH)	1.085	1.088
		r(SeH)	1.441	1.473
		$\angle$(CSeH)	94.9	95.5
		$\angle$(HCH)	109.0[c]	110.0[c]
O=C=Se	$C_{\infty v}$	r(CSe)	1.662	1.709
		r(CO)	1.168	1.157
LiBr[d]	$C_{\infty v}$	r(LiBr)	2.047	2.17
CH$_3$Br	C_{3v}	r(CBr)	1.918	1.933
		r(CH)	1.086	1.086
		$\angle$(HCH)	109.2	111.2
BrF	$C_{\infty v}$	r(BrF)	1.771	1.756
H$_3$SiBr	C_{3v}	r(SiBr)	2.205	2.210
		r(SiH)	1.422	1.451
		$\angle$(HSiH)	109.9	111.0
Br$_2$	$D_{\infty h}$	r(BrBr)	2.291	2.283

[a] Unless otherwise noted experimental data from: J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, "Structure Data on Free Polyatomic Molecules", Landolt-Bornstein, New Series, Group II, Vol. 7, K. H. Hellwege and A. M. Hellwege, Ed., Springer-Verlag, Berlin, 1976. Complete tabulation of structures of gaseous polyatomic molecules through mid 1974. Data on diatomic molecules, reviewed through 1972, may be found in volume 6 of this series. [b] Collapses to $D_{\infty h}$ symmetry. [c] Average value. [d] D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser. (U. S., Natl. Bur. Stand.)*, NSRDS-NBS 37 (1971).

imental data on other two heavy-atom molecules containing multiple bonds to a third-row element are unavailable. Our limited comparisons suggest that bonds involving two third-row elements are quite well described by the simple theory. Calculated bond lengths in digermane, in bromogermane, and in molecular bromine are close to their respective experimental values.

Equilibrium bond angles are also reasonably well described by the minimal basis-set calculations. Those in arsine and in hydrogen selenide are within 2° of their respective experi-

Table VI. Total Atomic and Molecular Energies (hartrees)

atom or molecule	STO-2G	STO-3G
K	−577.497 63	−593.076 16
Ca	−652.550 50	−669.989 19
Ga	−1853.709 74	−1900.728 50
Ge	−2000.624 21	−2051.636 26
As	−2154.649 72	−2209.263 67
Se	−2315.155 05	−2373.527 34
Br	−2482.409 09	−2544.636 78
Kr	−2656.480 29	−2722.706 00
KH		−593.573 02
GeH$_4$		−2054.090 25
AsH$_3$	−2156.385 05	−2211.014 03
SeH$_2$	−2316.306 36	−2374.692 43
HBr	−2482.992 85	−2545.156 06
KCN		−684.199 86
KOH		−667.396 30
CaF$_2$		−865.916 57
GeH$_3$CH$_3$		−2092.678 98
GeH$_3$CN		−2144.660 48
GeH$_3$F	−2097.612 71	−2151.549 41
GeH$_3$Cl		−2508.146 92
GeH$_3$GeH$_3$		−4107.061 50
GeH$_3$Br		−4598.228 88
AsF$_3$		−2504.361 03
H$_3$CSeH		−2413.277 44
O=C=Se		−2484.794 50
LiBr		−2552.086 82
CH$_3$Br		−2583.813 61
BrF		−2642.636 13
SiH$_3$Br		−2832.056 94
Br$_2$	−4964.888 41	−5089.184 53

Table VII. Comparison of Theoretical STO-2G, STO-3G, and Experimental Equilibrium Geometries

molecule	point group	geometric parameter	STO-2G	STO-3G	exptl[a]
AsH$_3$	C_{3v}	r(AsH)	1.447	1.456	1.511
		$\angle$(HAsH)	96.2	93.9	92.1
SeH$_2$	C_{2v}	r(SeH)	1.444	1.439	1.460
		$\angle$(HSeH)	94.4	92.4	90.6
HBr	$C_{\infty v}$	r(HBr)	1.421	1.414	1.415
GeH$_3$F	C_{3v}	r(GeF)	1.673	1.706	1.732
		r(GeH)	1.407	1.435	1.522
		$\angle$(HGeH)	110.0	110.8	113.0
Br$_2$	$D_{\infty h}$	r(BrBr)	2.274	2.291	2.283

[a] See footnote *a* of Table V for references to experimental data.

mental values. Experimental bond angles involving third-row atoms in more complicated molecules are reproduced to a comparable extent by the theory.

STO-2G Basis Sets. Poppinger[12] has recently demonstrated that the STO-2G minimal basis set yields equilibrium structures for molecules containing first-row atoms in good accord with those obtained from STO-3G. This observation is of considerable importance in light of recent developments in analytical methods for energy derivative calculations, the time for which depends to a greater extent on the total number of primitive Gaussians than on the total number of atomic basis functions. Whereas a single-point energy calculation at the STO-2G level requires half to a third the computer time as the corresponding STO-3G level calculations, evaluation of the gradient needed for geometry optimization, using the smaller basis set, is upwards of 3–4 times faster.

The STO-2G basis set we adopt assumes inner- and valence-shell scale factors identical with those determined appropriate for STO-3G. No attempt at reoptimization has been made.

STO-2G equilibrium geometries for a few of the molecules previously considered are presented in Table VII. They are

(12) D. Poppinger, *Chem. Phys.*, **12**, 131 (1976).

compared both to experimental structures and to those obtained at the STO-3G level. In all but two cases (SeH$_2$ and HBr) calculated STO-2G bond lengths are shorter than the corresponding STO-3G values; in every example considered, except SeH$_2$, are the STO-3G bond distances closer to experimental values. The most significant shortenings are for the GeF and GeH linkages in fluorogermane, reduced by 0.033 and 0.028 Å from their respective STO-3G values. Equally disturbing in the tabulated data are the calculated bond angles for SeH$_2$ and AsH$_3$, both of which are considerably larger than both the STO-3G and experimental values.

Conclusion

STO-3G minimal basis sets for the main group elements of the third row have been developed in a manner analogous to that employed for first- and second-row representations. Application of these basis sets to the calculation of the equilibrium structures of one and two heavy-atom molecules has been explored. Overall, the agreement between calculated (STO-3G) and experimental equilibrium structures is remarkable in view of the simplicity of the theoretical model. It suggests the utility of the method as a generally applicable means of structure determination for compounds involving main-group third-row elements.

Contribution from the Department of Chemistry, The University of Mississippi, University, Mississippi 38677

Lower Valence Fluorides of Vanadium. 5. Dependence of Structure and Magnetic Properties of Tetragonal K$_x$VF$_3$ on Composition

Y. S. HONG, R. F. WILLIAMSON, and W. O. J. BOO*

Ten samples of tetragonal tungsten bronze like K$_x$VF$_3$ of evenly spaced compositions between $x = 0.45$ and 0.56 were prepared and studied. Guinier–Hägg X-ray data showed an approximately linear dependence of sublattice dimensions on composition with $a = 12.190 + 0.815x$ and $c = 3.735 + 0.411x$. An orthorhombic superlattice was found to be independent of composition with dimensions $a(\text{super}) = 2^{3/2}a(\text{sub})$, $b(\text{super}) = 2^{1/2}a(\text{sub})$, and $c(\text{super}) = 2c(\text{sub})$. Magnetic measurements revealed K$_x$VF$_3$ to be ferrimagnetic (low x) and to change abruptly at $x = 0.49$ to antiferromagnetic (high x). The spontaneous moment of the ferrimagnetic phase depends on the field in which the sample is cooled. At large fields (10–12 kG) these moments approach the theoretical value $\sigma = x[g(V^{2+})S(V^{2+}) - g(V^{3+})S(V^{3+})]$. The vanadium ions occupy two lattice sites, 8j and 2c, in the tungsten bronze structure ($P4/mbm$), and the ferrimagnetic–antiferromagnetic behavior is explained by two mechanisms. In the ferrimagnetic phase, the mechanism for long-range order between vanadium ions on 8j sites does not include vanadium ions on 2c sites. In the antiferromagnetic phase, the vanadium ions on 2c sites are included in the ordering mechanism.

Introduction

The tetragonal system K$_x$VF$_3$ ($x = 0.45$–0.56) was reported to be a fluoride analogue of tetragonal tungsten bronze K$_x$WO$_3$, space group $P4/mbm$.[1-3] A superstructure was reported for K$_x$VF$_3$ in which the a dimension was increased by $2^{3/2}$ and the c dimension by 2.[1] Below the magnetic ordering temperature ($\sim$50 K) K$_x$VF$_3$ displays a strong ferrimagnetic moment at $x = 0.45$[1,4] and almost ideal antiferromagnetic behavior at $x = 0.56$.[1]

A ferrimagnet is defined as a substance in which two kinds of ions with magnetic moments of different magnitude are located on two distinct sublattices such that below the long-range magnetic ordering temperature the two moments are opposed, giving rise to a resultant spontaneous moment. This moment per magnetic ion can be expressed in Bohr magnetons as

$$\sigma = \tfrac{1}{2}[g(A)S(A) - g(B)S(B)]$$

where $g(A)$, $g(B)$, $S(A)$, and $S(B)$ are the Lande splitting factors and spin quantum numbers of ions A and B, respectively. A prerequisite for the two-sublattice model is that the two kinds of magnetic ions exist in an ordered arrangement. Consequently, a more detailed study of the spontaneous moments of K$_x$VF$_3$ should reveal important structural information. Toward this end, ten samples, designated as the "B" series, spanning the composition range $x = 0.450$–0.5625, were characterized and studied.

Experimental Section

The K$_x$VF$_3$ compounds were prepared by solid-state reactions as described previously for preparation of the "A" series.[1] In this work, the compounds are designated "B" series and were prepared in 1.91-cm diameter by 3.18-cm length molybdenum containers. Vacuum encapsulation was done by electron-beam welding at the University of Mississippi. Products were analyzed optically by stereoscopic and polarized microscopy. Chemical analyses were performed by Galbraith Laboratories. Vanadium was determined volumetrically, fluorine by specific ion electrode, and potassium by atomic absorption. Samples were characterized by Guinier–Hägg X-ray techniques using Cu Kα_1 and Cr Kα_1 radiations. Magnetic measurements were made from 4.2 to 300 K between 0.14 and 12 kG by using a Foner type PAR vibrating-sample magnetometer equipped with a Janis liquid helium Dewar, gallium arsenide temperature controller, and copper–constantan thermocouples. Magnetic fields were measured with a F. W. Bell hall-probe gaussmeter, Model 8860. Magnetic data were corrected for core diamagnetism, and an additional temperature-independent orbital paramagnetic correction of 6×10^{-4} cm^3 mol^{-1} was made for the V^{3+} ion.

(1) R. F. Williamson and W. O. J. Boo, *Inorg. Chem.*, **16**, 649 (1977).
(2) B. J. Garrard, B. M. Wanklyn, and S. H. Smith, *J. Cryst. Growth*, **22**, 169 (1974).
(3) C. Cros, R. Feurer, M. Pouchard, and P. Hagenmuller, *Rev. Chim. Miner.*, **11**, 585 (1974).
(4) C. Cros, R. Feurer, J. C. Grenier, and M. Pouchard, *Mater. Res. Bull.*, **11**, 539 (1976).