

# Compact Contracted Basis Sets for Third-Row Atoms: Ga–Kr

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Received 13 February 1990; accepted 7 May 1990

The (14s11p5d) primitive basis set of Dunning for the third-row main group atoms Ga–Kr has been contracted [6s4p1d]. The core functions have been relatively highly contracted while those which represent the valence region have been left uncontracted to maintain flexibility. Calculations with the [6s4p1d] contraction are reported for a variety of molecules involving third-row atoms. This basis set is found to satisfactorily reproduce experimental properties such as geometric configurations, dipole moments, and vibrational frequencies for a range of molecules. Comparisons are made with the performance of the uncontracted basis set. Polarization functions for the contracted basis set are reported and performance of the basis set with and without polarization functions is examined. A relaxation of the [6s4p1d] contraction to [9s6p2d] for higher level everygy calculations is also presented.

## INTRODUCTION

Basis sets for third-row nontransition metal atoms Ga–Kr are not nearly as well developed as those for first- and second-row atoms, although there is considerable interest, both experimentally and theoretically, in compounds and clusters containing these atoms. There are minimal<sup>1,2</sup> and split valence<sup>3</sup> basis sets for the third-row nontransition atoms that have been quite extensively tested. Dobbs and Hehre<sup>3</sup> reported a 3-21G<sup>(\*)</sup> basis which gave geometries in good agreement with experiment. They found *d*-polarization functions necessary to obtain good agreement with experiment in many cases. However, there is no well characterized full polarization basis set for these atoms analogous to the 6-31G\* and 6-311G\* basis sets for first- and second-row atoms,<sup>4,5</sup> i.e., small enough to be used in calculations on polyatomic molecules, large enough to yield reliable properties, and flexible enough to be used in calculations beyond Hartree–Fock (HF) theory. We have derived two new extended basis sets for the atoms

Ga–Kr with this purpose in mind. In this article we describe the two basis sets and present a systematic study of molecular properties obtained with the smaller of the two. Bond dissociation energies and ionization potentials of some one-heavy atom hydrides using the larger of the basis sets at the correlation level are presented elsewhere.<sup>6,7</sup>

There are several large uncontracted basis sets for the third-row nontransition metal atoms.<sup>8,9</sup> We have used the (14s11p5d) primitive set of Dunning<sup>8</sup> for Ga–Kr to derive the two new contracted basis sets. In the uncontracted form the (14s11p5d) primitive set produces atomic energies quite close to the Hartree–Fock limit; yet the number of primitive functions is small enough to make their use economical. Several studies<sup>10–13</sup> have shown that Dunning's (14s11p5d) primitive Gaussian basis set for Ga–Kr, both uncontracted and in various contractions, gives satisfactory results for specific species. The smaller of the two basis sets we report is a contraction of Dunning's set to [6s4p1d]. This is a compact contraction, dense in the core, flexible in the valence region, resulting in a basis set capable of calculating molecular properties such as geometries and vibrational frequencies. The second basis set was obtained by relaxation of the [6s4p1d] contraction to [9s6p2d]. Polarization and diffuse functions for these basis sets were also derived.

Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract No. W-31-109-ENG-38.

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In the second section the basis set contractions are presented along with polarization functions and diffuse *sp* functions for use with them. In the third section the performance of the [6*s*4*p*1*d*] basis set is examined in calculations at the Hartree–Fock level (restricted for closed shell species and unrestricted for open-shell) of geometries, harmonic vibration frequencies, and dipole moments for a broad selection of molecules containing third-row nontransition atoms for which experimental information is available. Among the classes treated are hydrides, oxides, hypervalents, and molecules with more than one third-row atom. Some calculations were also done with the uncontracted basis set to judge how well the contracted basis set reproduces the properties of the parent uncontracted basis set. Finally, conclusions are drawn concerning the use of the [6*s*4*p*1*d*] basis set in calculations of molecular properties.

## BASIS SET CONTRACTION

Methods for basis set contraction have been reviewed elsewhere.<sup>14,15</sup> We have used a simple segmented contraction of Dunning's<sup>8</sup> (14*s*11*p*5*d*) primitive Gaussian set. It is well known that contraction results in a poorer calculated total energy. The loss may be partially recovered by including some primitives in more than one contracted function or by employing a generalized contraction.<sup>16</sup> However, simple segmented contractions are the most widely used. We have done a simple segmented contraction with the idea that, although there is some energy loss, the properties of an uncontracted basis set can be retained in the contracted one provided the valence representation is flexible enough.

In the contractions reported here, initial guesses for the contraction coefficients were taken from expansion coefficients of uncontracted primitives<sup>8</sup> in HF calculations on the atomic ground states. The contraction coefficients were iteratively energy optimized both by group scaling and individually. Typically, five iterations produced coefficients converged to within 1% and a total atomic energy converged to within a millihartree. Neither an *s* = *p* or *s* = *p* = *d* constraint is present in the primitive set of Dunning. We have chosen not to implement such a constraint in our contracted basis sets because it probably would not save much time in correlation calculations where integral evaluation is a small part, and it is desirable to have a compact basis set.

Contraction of the (14*s*11*p*5*d*) primitive basis sets to [6*s*4*p*1*d*], referred to as the 641 basis, was straightforward. The 14*s* functions are grouped easily as (821111). Functions *s*<sub>1</sub> – *s*<sub>8</sub> comprise the

atomic 1*s* orbital, *s*<sub>9</sub> and *s*<sub>10</sub> the 2*s* orbital, with minor contributions to other atomic orbitals. The ratio *s*<sub>10</sub>/*s*<sub>9</sub> rises slightly in some molecular orbitals, but the contraction is valid. The four most diffuse *s* functions contribute in varying proportions to atomic and molecular orbitals and are left uncontracted to allow the basis freedom to adapt in differing environments. The 11*p* functions are more difficult to contract compactly. Contraction to [4*p*] is the largest set consistent with the goal of a compact basis. The best grouping for contraction to [4*p*] is (6311), but the [4*p*] contraction is not as invariant to environment as is the [6*s*]. The five *d* functions, on the other hand, group naturally. Ratios of expansion coefficients remain quite stable, although their behavior was not observed in hypervalent species. The exponents and coefficients of the 641 basis are listed in Table I. Atomic energies obtained from this basis are given in Table II.

Energetic performance of the 641 basis could be enhanced by including some primitive functions in more than one contracted function. Function *s*<sub>9</sub> could profitably be included in {*s*<sub>1–8</sub>}, and {*s*<sub>9,10</sub>} would benefit from inclusion of *s*<sub>7</sub>, *s*<sub>8</sub> and *s*<sub>11</sub>. The set {*p*<sub>1–6</sub>} would be aided by adding function *p*<sub>7</sub> and {*p*<sub>7–9</sub>} by adding functions *p*<sub>5</sub> and *p*<sub>6</sub>. But it is unlikely that any gains from these additions would be great enough to justify the increased complexity, nor would such additions significantly enhance the flexibility of the basis sets.

A second basis set was obtained by relaxation of the [6*s*4*p*1*d*] set to [9*s*6*p*2*d*]. In this basis set the 14*s* are grouped (61111111), the 11*p* are grouped (61111), and the 5*d* are grouped (41). This basis, referred to as 962, gives much lower energies than 641, much closer to the uncontracted set. The atomic energies from the 962 basis are listed in Table II along with the atomic energies from the uncontracted set. The 962 basis has been used along with the polarization functions described here to make accurate predictions of dissociation energies and ionization energies of a series of one-heavy atom hydrides.<sup>6,7</sup>

Reliable calculation of properties often requires adequately polarized basis sets. Therefore *d*- and *f*-polarization functions have been generated. The *d*-polarization functions are especially necessary to correctly predict geometries of molecules which contain third-row atoms. The 4*d* orbitals in these atoms, although unoccupied, are in the valence shell. Most of the calculations reported here have included a single *d*-polarization function (five uncontracted *d*-functions: *d*<sub>z<sup>2</sup></sub>, *d*<sub>xy</sub>, *d*<sub>yz</sub>, *d*<sub>x<sup>2</sup>–y<sup>2</sup></sub>, *d*<sub>xy</sub>) in the third-row atom basis. Polarization exponents for Ga–Kr are listed in Table III. The *d* and *f* polarization functions were optimized in HF calculations on the series of ground

state homonuclear diatomic molecules  $\text{Ga}_2 - \text{Kr}_2$  at their experimentally determined equilibrium bond distances.<sup>17</sup> There are no experimental bond-lengths for  $\text{Ge}_2$  and  $\text{Ga}_2$  so theoretical bondlengths were used.<sup>18</sup> The  $d$  function exponents were optimized using the  $[6s4p1d]$  basis on each atom,  $f$  exponents were optimized with the  $d$  polarization functions present. Molecule optimized exponents differed by as much as 10% from corresponding atom optimized exponents.

Diffuse  $sp$  exponents for Ga-Br are given in Table III. Diffuse exponents were derived for Ge, As, and Se on the basis of atomic calculations. Atomic energies were found to be quite insensitive to the exponent. On this basis, values of 0.02 are recommended for Ga and Br.

For atoms of the first and second rows, a pair of  $d$  polarization functions may be efficiently generated from a single one by doubling and halving the exponent of the single function, i.e., new exponents  $n\alpha_d$  and  $\alpha_d/n$  ( $n = 2$ ) are generated from exponent  $\alpha_d$ . For third-row hydrides,  $\text{AH}_n$  ( $A = \text{Ge, As, Se}$ ), this type of splitting of the

$d$  exponent increases the energy compared to that obtained with a single  $d$  function. We have found a more appropriate value of  $n$  to be 1.44. This is an average value based on energy optimizations of the saturated one-heavy-atom hydrides of Ge, As, and Se. The splitting of the  $d$  function, as well as the  $f$  polarization functions and diffuse  $sp$  functions, are not used in this study, but have been successfully employed in dissociation energy and ionization potential calculations on the one-heavy-atom hydrides.<sup>6,7</sup>

## RESULTS AND DISCUSSION

In this section we present calculations of equilibrium geometries, harmonic vibration frequencies and dipole moments for a large number of species for which experimental data are available. In most calculations we use the 641 basis set augmented with a  $d$  polarization function, exponents of which are given in Table III. This basis is referred to as 641( $d$ ). The hydrogen basis used

**Table I.**  $[6s4p1d]$  basis sets for Ga-Kr contracted from the  $(14s11p5d)$  primitive Gaussian sets

Ga		Ge		As	
Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient
<i>s</i>		<i>s</i>		<i>s</i>	
457600.0	0.00022088	489000.	0.000222	526200.	0.000220
68470.0	0.0017224	73100.	0.001728	78310.	0.00172
15590.0	0.0088661	16640.	0.008950	17800.	0.00889
4450.0	0.035919	4742.	0.035905	5070.	0.03535
1472.0	0.11446	1569.	0.11284	1677.	0.11226
541.3	0.28163	577.	0.28748	617.	0.28625
214.8	0.44810	229.	0.43449	245.	0.43406
88.81	0.29552	94.81	0.30683	101.5	0.30880
27.18	0.48025	29.22	0.47759	31.39	0.47299
11.54	1.14780	12.45	1.11445	13.43	1.12375
3.303	1.0	3.642	1.0	4.0	1.0
1.334	1.0	1.502	1.0	1.683	1.0
0.1947	1.0	0.2462	1.0	0.3003	1.0
0.07158	1.0	0.09209	1.0	0.1137	1.0
<i>p</i>		<i>p</i>		<i>p</i>	
3274.0	0.0014743	3596.	0.001442	3909.	0.00133
765.4	0.013270	843.7	0.012442	924.	0.01140
241.6	0.065384	266.2	0.064694	291.8	0.05981
89.39	0.22961	98.28	0.21866	107.5	0.20511
36.36	0.39929	39.93	0.39335	43.62	0.37432
15.60	0.43593	17.14	0.43453	18.73	0.42141
6.472	0.26105	7.157	0.24998	7.841	0.21901
2.748	0.48347	3.068	0.46938	3.391	0.42955
1.090	0.28721	1.246	0.28896	1.405	0.26400
0.2202	1.0	0.2795	1.0	0.3441	1.0
0.06130	1.0	0.08340	1.0	0.1068	1.0
<i>d</i>		<i>d</i>		<i>d</i>	
59.66	0.031960	70.18	0.02877	81.59	0.02558
17.10	0.16358	20.07	0.15525	23.26	0.14492
6.030	0.36720	7.059	0.36814	8.148	0.36044
2.171	0.45704	2.553	0.46578	2.954	0.46255
0.6844	0.30477	0.8301	0.28648	0.9827	0.26813

**Table I.** (continued)

Se		Br		Kr	
Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient
<i>s</i>		<i>s</i>		<i>s</i>	
560600.	0.000220	574300.	0.0002204	605700.	0.00022997
84010.	0.00170	89070.	0.0016871	90300.	0.0017432
19030.	0.00883	20210.	0.087457	20920.	0.0090459
5419.	0.03508	5736.	0.035597	5889.	0.036901
1792.	0.11266	1899.	0.11352	1950.	0.11743
659.5	0.28471	698.7	0.27973	718.2	0.28617
262.	0.43348	277.8	0.44938	285.4	0.45408
108.6	<u>0.31140</u>	115.2	<u>0.30023</u>	118.6	<u>0.28501</u>
33.66	0.46823	35.97	0.45726	38.16	0.46465
14.45	<u>1.09261</u>	15.50	<u>1.22978</u>	16.45	<u>1.24448</u>
4.378	<u>1.0</u>	4.771	<u>1.0</u>	5.221	<u>1.0</u>
1.876	<u>1.0</u>	2.077	<u>1.0</u>	2.291	<u>1.0</u>
0.3592	<u>1.0</u>	0.4211	<u>1.0</u>	0.4837	<u>1.0</u>
0.1367	1.0	0.1610	1.0	0.1855	1.0
<i>p</i>		<i>p</i>		<i>p</i>	
4114.	0.00117	4406.	0.0013766	4678.	0.0013437
980.4	0.00985	1042.	0.012207	1120.	0.011821
310.7	0.05177	332.1	0.060190	357.1	0.058277
114.2	0.17869	121.9	0.22370	131.4	0.21854
46.26	0.32504	49.24	0.40047	52.86	0.39757
19.87	<u>0.36089</u>	21.16	<u>0.44458</u>	22.70	<u>0.44119</u>
8.309	0.21488	8.836	0.27245	9.547	0.26887
3.598	0.39629	3.829	0.49469	4.167	0.49381
1.522	<u>0.22508</u>	1.643	<u>0.25684</u>	1.811	<u>0.25069</u>
0.4032	<u>1.0</u>	0.465	<u>1.0</u>	0.5337	<u>1.0</u>
0.1231	1.0	0.1427	1.0	0.1654	1.0
<i>d</i>		<i>d</i>		<i>d</i>	
94.03	0.02063	108.4	0.021521	125.6	0.015695
26.79	0.12227	30.71	0.13376	35.31	0.10301
9.336	0.31972	10.66	0.36673	12.15	0.29968
3.383	0.41738	3.851	0.49037	4.35	0.41171
1.145	0.23184	1.317	0.26749	1.494	0.21548

with the 641(*d*) basis is a (4*s*) set contracted to [2*s*].<sup>19</sup> The 6-31G\* basis<sup>4</sup> is used for the first- and second-row atoms in the compounds. Tables IV–VIII present the results of the calculations including the principal hydrides of each of the third-row atoms (Table IV), diatomic oxides (Table V), homonuclear third row diatomics (Table VI), polyatomics (Table VII), and hypervalent molecules (Table VIII). For the principal hydrides and the diatomic oxides calculations have also been done with the uncontracted (14*s*11*p*5*d*) basis sets for

comparison with the contracted set. These results are also included in the tables.

Calculations on the hydrides in Table IV have been done using the 641 and 641(*d*) basis sets. Calculations were also carried out using the uncontracted (14*s*11*p*5*d*) basis set with and without *d* polarization functions. Calculations with the four basis sets are used to compare the performance of the contracted basis sets with the uncontracted and of polarized basis sets with unpolarized. Comparison of results achieved with a

**Table II.** Atomic energies (in Hartrees).

Atom	Basis Sets					
	641	641( <i>d</i> )	962	962( <i>d</i> )	(14 <i>s</i> 11 <i>p</i> 5 <i>d</i> )	(14 <i>s</i> 11 <i>d</i> 5 <i>d</i> ) ( <i>d</i> )
Ga( <sup>2</sup> P)	−1921.06770	−1921.07965	−1923.02732	−1923.04070	−1923.17919	−1923.19266
Ge( <sup>3</sup> P)	−2072.92774	−2072.96147	−2075.10160	−2075.11440	−2075.28080	−2075.29369
As( <sup>4</sup> P)	−2231.62732	−2231.63806	−2233.96069	−2233.96994	−2234.15988	−2234.16934
Se( <sup>3</sup> P)	−2397.09911	−2397.11204	−2399.57613	−2399.58739	−2399.78859	−2399.79995
Br( <sup>2</sup> P)	−2569.56144	−2569.57128	−2572.15424	−2572.16519	−2572.35936	−2572.37038
Kr( <sup>1</sup> S)	−2748.97320	−2748.97969	−2751.74193	−2751.74948	−2751.96707	−2751.97144

**Table III.** Polarization and diffuse function exponents for Ga–Kr.

	Ga	Ge	As	Se	Br	Kr
$d$	0.141	0.202	0.273	0.315	0.338	0.318
$f$	0.167	0.267	0.372	0.400	0.401	— <sup>a</sup>
diffuse <sup>b</sup>	0.02	0.019	0.021	0.022	0.02	—

<sup>a</sup>A suitable  $f$  exponent for Kr could not be determined from calculations on Kr<sub>2</sub> due to the long bond distance.<sup>b</sup>Diffuse  $sp$  function exponents.**Table IV.** Calculated and experimental properties of the principal hydrides of the third-row main group elements Ga–Kr.

Molecule	Basis <sup>a</sup>	Geometry <sup>b</sup>		Frequencies, cm <sup>-1c, d</sup>				Dipole moment (D) <sup>e</sup>	Energy (Hartrees)
		AH	HAH	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$		
GaH ( $C_{\infty v}$ )	3-21G(*)	1.695						0.3	–1914.55027
	641	1.676		1694				0.33	–1921.63951
	(14s11p5d)	1.668		1692				0.24	–1923.75200
	641 ( $d$ )	1.676		1685				0.18	–1921.65267
	(14s11p5d) ( $d$ )	1.674		1668				0.09	–1923.76543
	Expt.	1.663		1605				—	
GeH <sub>4</sub> ( $T_d$ )	3-21G(*)	1.546							–2067.81435
	641	1.535		2264	987	2240	899		–2075.28159
	(14s11p5d)	1.526		2283	999	2252	916		–2077.61714
	641 ( $d$ )	1.537		2251	1000	2240	903		–2075.31025
	(14s11p5d) ( $d$ )	1.533		2254	998	2233	907		–2077.63755
	Expt.	1.525		2106	931	2214	819		
AsH <sub>3</sub> ( $C_{3v}$ )	3-21G(*)	1.522	93.3	2353	1017	2354	1122	0.6	–2225.34712
	641	1.513	95.4	2307	1131	2294	1012	0.91	–2233.32722
	(14s11p5d)	1.503	95.0	2331	1145	2313	1038	0.68	–2235.86664
	641 ( $d$ )	1.511	94.1	2360	1129	2362	1021	0.65	–2233.36644
	(14s11p5d) ( $d$ )	1.510	93.9	2345	1129	2343	1029	0.51	–2235.89484
	Expt.	1.511	92.1	2116	1003	2123	906	0.2	
H <sub>2</sub> Se ( $C_{2v}$ )	3-21G(*)	1.464	92.1	2591	1192	2600		1.0	–2389.83430
	641	1.465	94.3	2479	1174	2484		1.43	–2398.24489
	(14s11p5d)	1.454	93.8	2509	1197	2512		1.22	–2400.93892
	641 ( $d$ )	1.458	92.8	2593	1188	2602		1.00	–2398.28128
	(14s11p5d) ( $d$ )	1.458	92.6	2573	1191	2580		0.92	–2400.96660
	Expt.		1.460	90.6	2345	1034	2358	0.24	
HBr ( $C_{\infty v}$ )	3-21G(*)	1.417		2802				1.1	–2560.84279
	641	1.426		2630				1.51	–2570.14558
	(14s11p5d)	1.415		2657				1.36	–2572.94520
	641 ( $d$ )	1.416		2788				1.13	–2570.16893
	(14s11p5d) ( $d$ )	1.415		2764				1.06	–2572.96637
	Expt.	1.414		2649				0.8	
KrH <sup>+</sup> ( $C_{\infty v}$ )	641	1.436		2352				2.78	–2749.10129
	(14s11p5d)	1.422		2393				2.57	–2752.09723
	641 ( $d$ )	1.430		2553				2.09	–2749.12995
	(14s11p5d) ( $d$ )	1.427		2535				2.02	–2752.12362
	Expt. <sup>f</sup>	1.50		2495				—	

<sup>a</sup>Basis sets described in text. (14s11p5d) is the uncontracted primitive basis set; (14s11p5d) ( $d$ ) is the uncontracted set with a  $d$  polarization function; the contracted hydrogen basis is used in all calculations. 3-21G(\*) results are from reference 3.<sup>b</sup>Bond distances in Å, bond angles in degrees. Experimental geometries of diatomics from reference 17. Experimental geometries of polyatomics from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Structure Data of Free Polyatomic Molecules*, Landolt-Bornstein, New Series, Group II, Springer-Verlag, Berlin, 1976, V. 7.<sup>c</sup>Theoretical frequencies are harmonic vibrational frequencies. Experimental frequencies of diatomics are harmonic frequencies; those of polyatomics are fundamentals.<sup>d</sup>Except as noted, experimental vibrational frequencies of diatomic molecules are from reference 17. Those of polyatomics are from T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Vol. I*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (US) 39 (1972).<sup>e</sup>Experimental dipole moments are from A. L. McClellan, *Tables of Experimental Dipole Moments, Vol. 2*, Rahrar Enterprises, El Cerrito, CA (1974).<sup>f</sup>J.W.C. Johns, *J. Mol. Spectrosc.*, **106**, 124 (1984).

**Table V.** Calculated and experimental properties of diatomic third-row oxides.<sup>a,b</sup>

Molecule	Basis	$R_e$ , Å	Frequency (cm <sup>-1</sup> )	Dipole Moment (D)	Energy (Hartrees)
GaO ( <sup>2</sup> Σ)	641 ( <i>d</i> )	1.801	639	3.01	-1995.92203
	(14s11p5 <i>d</i> ) ( <i>d</i> )	1.790	636	2.99	-1998.03473
	Expt.	1.744	768	—	—
GeO ( <sup>1</sup> Σ <sup>+</sup> )	3-21G(*)	1.619		3.5	-2139.96923
	641( <i>d</i> )	1.603	1124	3.74	-2147.85236
	(14s11p5 <i>d</i> ) ( <i>d</i> )	1.593	1142	3.75	-2150.18650
	Expt.	1.625	986	3.27	—
AsO ( <sup>2</sup> Π)	641( <i>d</i> )	1.594	1148	3.14	-2306.44976
	(14s11p5 <i>d</i> ) ( <i>d</i> )	1.584	1152	3.19	-2308.98163
	Expt.	1.624	967	—	—
SeO ( <sup>3</sup> Σ <sup>-</sup> )	641( <i>d</i> )	1.614	1076	2.36	-2471.93268
	(14s11p5 <i>d</i> ) ( <i>d</i> )	1.604	1069	2.44	-2474.62055
	Expt.	1.648	915	—	—
BrO ( <sup>2</sup> Π)	641( <i>d</i> )	1.783	639	1.17	-2644.34880
	(14s11p5 <i>d</i> ) ( <i>d</i> )	1.777	630	1.25	-2647.14696
	Expt.	1.717	779	1.76, 1.61	—

<sup>a</sup>See footnotes a–e of Table III.<sup>b</sup>The contracted 6-31G\* oxygen basis is used in both basis sets.**Table VI.** Theoretical and experimental<sup>a</sup> properties of third-row diatomic molecules.

Molecule	Basis <sup>b</sup>	$R_e$ , (Å)	$\omega_e$ , (cm <sup>-1</sup> )	Energy (Hartrees)
Ga <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	641	2.782	156	-3842.16011
	641( <i>d</i> )	2.728	174	-3842.18868
	Experiment <sup>c</sup>	—	180	—
As <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	641	2.110	472	-4463.22446
	641( <i>d</i> )	2.057	524	-4463.29712
	Experiment	2.103	430	—
Se <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	641	2.245	371	-4794.20137
	641( <i>d</i> )	2.141	446	-4794.27599
	Experiment	2.166	385	—
Br <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	641	2.437	305	-5139.12082
	641( <i>d</i> )	2.296	350	-5139.16648
	Experiment	2.281	325	—
Kr <sub>2</sub> <sup>d</sup> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	641	4.602	9	-5497.99643
	641( <i>d</i> )	4.053	25	-5498.15884
	Experiment	4.03	24	—
GeSe <sup>e</sup> ( <sup>1</sup> Σ <sup>+</sup> )	3-21G(*)	2.121		-4454.25783
	641	2.177	408	-4470.11660
	641( <i>d</i> )	2.124	451	-4470.17908
	Experiment	2.135	409	—

<sup>a</sup>Experimental quantities taken from reference 17 unless otherwise noted.<sup>b</sup>Basis sets described in text. 3-21G(\*) results are from reference 3.<sup>c</sup>F. W. Froben, W. Schulze, and V. Kloss, *Chem. Phys. Lett.*, **99**, 500 (1983).<sup>d</sup>MP2 theory used in optimizations rather than HF. No minimum was found for the 641(*d*) basis set at the HF level.<sup>e</sup>Calculated dipole moments are 3.20 D (641 basis) and 2.21 D (641(*d*) basis). Experimental dipole moment is 1.65 D.

contracted basis set with results obtained with its parent primitive set is done because some experimental properties, e.g., bond lengths and dipole moments, are not correctly represented even at the HF limit and direct comparison of properties calculated with both contracted and uncontracted basis sets indicates the extent to which contraction has altered the properties of the original basis set. It was not feasible to perform every cal-

culation documented here with uncontracted basis sets, but the hydrides are small enough to do so.

The results in Table IV indicate that calculated bond lengths and bond angles are in good agreement with experiment for each basis. Mean absolute deviation from experimental bond lengths, excluding KrH<sup>+</sup>, are 0.004 Å with the uncontracted basis (14s11p5*d*) basis, both with and

Table VII. Calculated and experimental properties of third-row polyatomic molecules.<sup>a</sup>

Molecule	Parameter	Geometry <sup>b</sup>		Vibration	Frequencies <sup>c</sup>		Dipole Moment (D)		Energy (Hartrees)
		Calc.	Exptl. <sup>d</sup>		Calc.	Exptl. <sup>e,f</sup>	Calc.	Exptl. <sup>g</sup>	
AsF <sub>3</sub> (C <sub>3v</sub> )	AsF	1.692	1.710	a <sub>1</sub>	834	738	2.49	2.65	-2530.02993
	FAsF	95.5	96.0	a <sub>1</sub>	379	337			
				e	809	699			
AsCl <sub>3</sub> (C <sub>3v</sub> )	AsCl	2.169	2.160	a <sub>1</sub>	443	416	1.78	2.1	
	ClAsCl	98.8	98.9	a <sub>1</sub>	218	192			
				e	420	391			
AsBr <sub>3</sub> (C <sub>3v</sub> )	AsBr	2.334	2.324	a <sub>1</sub>	309	272	1.28	1.66	-9940.50467
	BrAsBr	100.0	99.6	a <sub>1</sub>	143	128			
				e	310	287			
GeH <sub>3</sub> F <sup>h</sup> (C <sub>3v</sub> )	GeH	1.533	1.523	a <sub>1</sub>	2276	2121	2.15		-2174.20984
	GeF	1.726	1.734	a <sub>1</sub>	949	859			
	HGeF	107.0	106.0	a <sub>1</sub>	766	689			
GeH <sub>3</sub> Cl <sup>i</sup> (C <sub>3v</sub> )	GeH	1.530	1.521	e	2268	2132			-2534.26208
	GeCl	2.174	2.149	e	948	874			
	HGeCl	107.0	107.0	e	691	643	2.48	2.10	
				a <sub>1</sub>	2281	2121			
				a <sub>1</sub>	921	848			
				a <sub>1</sub>	431	423			
				e	2280	2129			
				e	952	874			
				e	643	602			

GeH <sub>3</sub> Br (C <sub>3v</sub> )	GeH	1.530	1.527	a <sub>1</sub>	2277	2116	2.18	2.00	-4644.37812
	GeBr	2.324	2.297	a <sub>1</sub>	914	833			
	HGeBr	107.4	106.3	a <sub>1</sub>	318	305			
				e	2277	2127			
Ga <sub>2</sub> O (C <sub>2v</sub> )	GaO	1.798	1.824	e	952	871			
	GaOGa	180.0	142.9	e	625	578			
				σ <sub>g</sub>	316	472	0	—	-3917.15724
				σ <sub>u</sub>	882	809			
Ge <sub>2</sub> H <sub>6</sub> <sup>f</sup> (D <sub>3d</sub> )	GeGe	2.445	2.403	π <sub>u</sub>	79	—			
	GeH	1.539	1.541				0	0	-4149.49103
	GeGeH	110.6	112.5						

<sup>a</sup>HF/641(d) results.<sup>b</sup>Bond lengths in Å, angles in degrees.<sup>c</sup>Frequencies in cm<sup>-1</sup>. Theoretical frequencies are harmonic vibrational frequencies, experimental are observed fundamentals.<sup>d</sup>Experimental geometries taken from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Structure Data of Free Polyatomic Molecules*, Landolt-Bornstein, New Series, Group II, Springer-Verlag, Berlin, Vol. 7.<sup>e</sup>Frequencies of AsF<sub>3</sub>, AsCl<sub>3</sub>, and AsBr<sub>3</sub> from K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed. Wiley, New York (1986).<sup>f</sup>Experimental frequencies for GeH<sub>3</sub>F, GeH<sub>3</sub>Cl, and GeH<sub>3</sub>Br from D. E. Freeman, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.* **39**, 2908 (1963).<sup>g</sup>Experimental dipole moments from A. L. McClellan, *Tables of Experimental Dipole Moments*, Vol. 2, Rahara Enterprises, El Cerrito, California (1974).<sup>h</sup>3-21G(\*) geometry of GeH<sub>3</sub>F (reference 3): GeH = 1.543 Å, GeF = 1.725 Å, <HGeH = 112.0°.<sup>i</sup>3-21G(\*) geometry of GeH<sub>3</sub>Cl (reference 3): GeH = 1.539 Å, GeCl = 2.178 Å, <HGeH = 112.0°.<sup>j</sup>3-21G(\*) geometry of Ge<sub>2</sub>H<sub>6</sub> (reference 3): GeH = 1.549 Å, GeGe = 2.447 Å, <GeGeH = 110.3°.



**Table VIII.** Calculated and experimental properties of third-row hypervalent molecules.<sup>a</sup>

Molecule	Parameter	Geometry <sup>b</sup>			Vibration	Frequencies <sup>c</sup>		Energy (Hartrees)
		Calc.	3-21G(*) (ref. 3)	Exptl. <sup>d</sup>		Calc.	Exptl. <sup>e</sup>	
SeO <sub>2</sub> (C <sub>2v</sub> )	SeO	1.575	1.599	1.608	a <sub>1</sub>	1127	922	-2546.72560
	OSeO	114.3	114.4	113.8	a <sub>1</sub>	433	372	
					b <sub>2</sub>	1181	966	
SeF <sub>4</sub> (C <sub>2v</sub> )	SeF	1.747	1.742	1.771	a <sub>1</sub>	857	739	-2794.78958
	SeF'	1.670	1.687	1.682	a <sub>1</sub>	668	551	
	FSeF	165.2	166.1	169.2	a <sub>1</sub>	419	362	
	F'SeF'	102.1	101.0	100.55	a <sub>1</sub>	182	200	
					a <sub>2</sub>	420	—	
					b <sub>1</sub>	855	585	
					b <sub>1</sub>	286	254	
					b <sub>2</sub>	724	717	
BrF <sub>3</sub> <sup>f</sup> (C <sub>2v</sub> )	BrF	1.701	1.721	1.728	a <sub>1</sub>	818	672	-2867.65677
	BrF'	1.787	1.778	1.809	a <sub>1</sub>	651	547	
	FBrF'	84.8	84.4	85.0	a <sub>1</sub>	294	235	
					b <sub>1</sub>	282	252	
					b <sub>2</sub>	689	597	
					b <sub>2</sub>	409	347	
AsF <sub>5</sub> (D <sub>3h</sub> )	AsF <sub>ax</sub>	1.683	1.694	1.711	a <sub>1</sub> '	826	733	-2728.89831
	AsF <sub>eq</sub>	1.658	1.672	1.656	a <sub>1</sub> '	737	642	
					a <sub>2</sub> '	887	785	
					a <sub>2</sub> '	431	400	
					e'	926	809	
						386	366	
						153	128	
					e''	388	407	
KrF <sub>2</sub> (D <sub>∞h</sub> )	KrF	1.836	1.826	1.875	σ <sub>g</sub>	620	449	-2947.56979
					π <sub>u</sub>	289	233	
					σ <sub>u</sub>	655	580,596	

<sup>a</sup>HF/641(d) results.<sup>b</sup>Bond lengths in Å, angles in degrees.<sup>c</sup>Frequencies in cm<sup>-1</sup>, theoretical frequencies are harmonic vibration frequencies, experimental are observed fundamentals.<sup>d</sup>See footnote d, Table VII.<sup>e</sup>Except as noted, from K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York (1986).<sup>f</sup>One BrF bond, two BrF' bonds.

without *d* polarization functions, 0.006 Å with the 641(*d*) basis, and 0.008 Å with the 641 basis. The bond length of KrH<sup>+</sup> is excluded because it is not experimentally as well characterized as those of the other hydrides.<sup>17</sup> The calculated bond angles of AsH<sub>3</sub> and H<sub>2</sub>Se are too large by about 2° at the 641(*d*) level. Similar results are obtained with the uncontracted basis. The errors are about 3–4° without the *d* polarization functions.

In those cases where there is an experimental dipole moment the calculated dipole moments are too large, typical of extended basis set calculations for first and second row compounds.<sup>20</sup> The results of the contracted basis set are close to those of the uncontracted results and inclusion of *d* polarization functions results in improved agreement with experiment.

With few exceptions the vibrational frequencies of the hydrides in Table IV are all overesti-

mated. The average absolute deviations of the 641 and 641(*d*) basis sets are 7% and 10%, respectively. This is typical for Hartree-Fock calculations of vibrational frequencies.<sup>21</sup> The uncontracted basis sets give similar deviations. In GeH<sub>4</sub> none of the basis sets correctly calculates the asymmetric stretching frequency higher than the symmetric, in AsH<sub>3</sub> both of the polarized basis sets correctly calculates the stretching frequencies as approximately equal, and in H<sub>2</sub>Se all basis sets are able to calculate the two stretching frequencies as being almost equal with the asymmetric stretch slightly higher.

The results of HF/641(*d*) calculations on the diatomic third row oxides, except KrO, are given in Table V. Also included in the table are results from the uncontracted (14s11p5*d*) basis with a *d* polarization function, i.e., (14s11p5*d*)(*d*). Although the total energies obtained with the

641(*d*) basis sets are 2–3 Hartrees above those obtained with the uncontracted sets, values of the properties are close. The 641(*d*) basis yields bond lengths which are only about 0.01 Å longer than those obtained with the uncontracted basis. For AsO, SeO, and GeO calculated bond lengths are shorter than experimental; for GaO and BrO, they are longer with both basis sets. The average absolute deviation is 0.04 Å at the HF/641(*d*) level with the largest errors being BrO (0.066 Å) and GaO (0.057 Å). Harmonic vibrational frequencies obtained from the 641(*d*) and uncontracted basis sets differ by an average of only 8 cm<sup>-1</sup>. The frequencies for GeO, AsO, and SeO are overestimated by an average of 16% while those of BrO and GaO are underestimated by an average of 17%.

Results of calculations on third-row diatomics are given in Table VI. Five homonuclear diatomics were considered as well as the heteronuclear diatomic germanium selenide. Germanium dimer was not included because of the paucity of available experimental data. Since krypton dimer is a van der Waals molecule, the optimization was done at the second-order perturbation theory (MP2) level.<sup>22</sup> All calculations were done with both the 641 and the 641(*d*) basis sets. With the two-heavy-atom diatomics, the effect of basis set polarization is evident in the calculated geometries. Bond lengths computed with the 641 basis sets are significantly longer than those computed with the 641(*d*). In Se<sub>2</sub> and Br<sub>2</sub> they are 0.05 and 0.14 Å longer, respectively. The absolute average deviation for the 641(*d*) basis is 0.024 Å. The HF/641(*d*) vibrational frequencies are in reasonable agreement with the experiment with an average absolute deviation of 10%. The 641 vibrational frequencies are off by about 16%. The 641(*d*) basis set, with correlation effects included at the MP2 level, gives very good agreement with experiment for the bondlength and vibrational frequency of Kr<sub>2</sub> despite the weak interaction.

The results of HF/641(*d*) calculations on AsX<sub>3</sub> (*X* = F, Cl, Br), GeH<sub>3</sub>X (*X* = GeH<sub>3</sub>, F, Cl, and Br), and Ga<sub>2</sub>O are given in Table VII. The calculated properties of these molecules are in quite good agreement with experiment. Calculated bond lengths are within 0.02 Å of experiment with the exception of the Ge—Ge bond in Ge<sub>2</sub>H<sub>6</sub> which is off by 0.04 Å and bond angles agree to within about one degree with the exception of Ga<sub>2</sub>O where theory indicates it to be linear and experiment gives an angle of 143°. The average absolute deviation from experiment of all vibrational frequencies in Table VII is 9.8%. The results for the AsX<sub>3</sub> and GeX<sub>3</sub>H series indicate that the properties (bondlengths, bondangles, and vibrational frequencies) of AsBr<sub>3</sub> and GeBrH<sub>3</sub> are described as well as those of the chloro- and

fluoro-species which use the 6-31G\* basis for the halogen atom. The geometry of Ge<sub>2</sub>H<sub>6</sub> is correctly calculated to be *D*<sub>3d</sub> with a barrier to rotation about the Ge—Ge bond of 0.7 kcal/mol.

In Table VIII the results of calculations on hypervalent molecules of the third row elements are presented. The calculated geometries again are in good agreement with experiment. Only one of the angles (FSeF in SeF<sub>4</sub>) deviates significantly from the experiment. In general the vibrational frequencies are calculated to be consistently higher than experimental, with an average absolute deviation of 17%. The larger deviation than for the polyatomics in Table VII may be due to difficulties with the hypervalency of these compounds.

Fifteen of the molecules in Tables IV–VIII were also considered by Dobbs and Hehre<sup>3</sup> in their testing of the 3-21G and 3-21G<sup>(\*)</sup> basis sets. The 3-21G<sup>(\*)</sup> optimized parameters are given in the tables for comparison with our results. Overall, for the 15 species, the differences with experiment are very similar for the two basis sets. The average deviation on bondlengths and bond angles was 0.017 Å and 1.5°, respectively, for the 641(*d*) basis and 0.018 Å and 1.3°, respectively, for the 3-21G<sup>(\*)</sup> basis set.

## CONCLUSIONS

We have described two new contracted basis sets for the atoms Ga through Kr derived from Dunning's<sup>8</sup> (14s11p5d) primitive set. The following conclusions can be drawn from the systematic study of the geometries, vibrational frequencies and dipole moments of the third-row nontransition metal compounds presented here using the 641(*d*) basis set.

1. Calculated HF/641(*d*) geometries are in good agreement with experiment. The average absolute deviation of 35 bondlengths is 0.022 Å and the average absolute deviation for 13 bond angles is 1.2°. The bond angle result excludes the Ga<sub>2</sub>O result where experiment indicates a GaOGa bondangle of 143° and theory gives a linear GaOGa bond angle.
2. The contracted 641 set gives properties that are in very good agreement with the uncontracted set despite being 2–3 Hartrees higher in energy. The *d* polarization functions are found to be very important to obtaining accurate properties in many cases as was found by Dobbs and Hehre<sup>3</sup> in their comparison of the 3-21G and 3-21G<sup>(\*)</sup> basis sets.
3. Vibrational frequencies calculated with the 641(*d*) basis are within about 10% of the experimental fundamental frequencies and are usually overestimated. This is similar to the performance of the 6-31G\* basis set.<sup>21</sup> The ex-

ceptions to this are the diatomic oxides and hypervalent compounds where the average deviation is about 17%. Calculated dipole moments are generally within about 0.5 D of experiment.

4. Fifteen species that were done in this study were also considered by Dobbs and Hehre<sup>3</sup> in their development of a smaller extended basis set for third-row nontransition atoms. Comparison of the results indicate that both the 641(*d*) and the 3-21G(\*) basis sets give comparable results for the geometries of these species. However, the 641(*d*) basis set gives atomic energies that are 7 to 9 Hartrees lower and should be useful in cases where a larger basis set is needed, such as in correlation calculations and in weak interactions.

In two other studies<sup>6,7</sup> we have tested the second and larger basis set presented here, the [9s6p2d] contracted basis, in correlation level calculations. This basis set gives energies which are only 0.2 hartrees higher than the uncontracted set. It was used, along with polarization and diffuse functions described here, to calculate dissociation energies and ionization potentials of AH<sub>n</sub> hydrides containing third-row nontransition atoms Ge-Se. Geometries for this study were obtained with the 641(*d*) basis at the Hartree-Fock level and correlation effects were included by Møller-Plesset perturbation theory. The dissociation energies and ionization potentials were within 3 kcal/mol of accurate experimental values.

This work was supported by the U.S. Department of Energy, Office of Basis Energy Sciences, Division of Materials Sciences, under Contract No. W-31-109-ENG-38.

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