J. Phys. Chem. A **1997,** *101,* 8701−8705

Assessment of Modified Gaussian-2 (G2) and Density Functional Theories for Molecules Containing Third-Row Atoms Ga−Kr[†]

P. C. Redfern, J.-P. Blaudeau, and L. A. Curtiss*

Chemical Technology Division/Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

Received: May 2, 1997; In Final Form: July 30, 1997⊗

The performance of G2(MP2) and G2(MP2,SVP) theories for molecules containing third-row nontransition elements Ga−Kr is assessed. The average absolute deviation from experiment for 40 test energies is 1.92 kcal/mol for both methods compared to 1.37 kcal/mol for G2 theory. Four density functional theories (BPW91, BLYP, B3PW91, and B3LYP) are also assessed for the 40 test energies and found to have average absolute deviations of 3.58, 4.75, 2.03, and 2.62 kcal/mol, respectively. The B3PW91 density functional theory gives the best agreement with experiment in contrast to first- and second-row systems, where B3LYP does better than B3PW91. Of the four density functional methods, the B3PW91 method gave the best agreement with experiment for geometries and is about as accurate as second-order perturbation theory.

I. Introduction

In a previous paper we extended Gaussian-2 (G2) theory[1] to third-row atoms Ga−Kr.[2] The final total energies are effectively at the QCISD(T)/6-311+G(3df,2p) level, making certain assumptions about the additivity of the corrections. Spin−orbit corrections for atoms and molecules having both spatially and spin degenerate states (^{2}P, ^{3}P for atoms and $^2\Pi$ for molecules) are included in the G2 energies. G2 theory for the third row was tested on a total of 40 energies (atomization energies, ionization energies, electron affinities, and proton affinities) having well-established experimental values and was found to have an average absolute deviation of 1.37 kcal/mol.

In this paper, two variants of G2 theory that have been proposed for first- and second-row elements are assessed on the 40 test energies used for the third row. In the first variant, referred to as G2(MP2) theory,[3] the basis set extensions of G2 theory are obtained using second-order Møller−Plesset perturbation theory (MP2). In the second variant, referred to as G2(MP2,SVP) theory, the QCISD(T) calculation in G2(MP2) theory is done using the 6-31G(d) basis set instead of the 6-311G(d,p) basis set.[4,5] Both of these methods give somewhat larger average absolute deviations with experiment than G2 theory for first- and second-row molecules,[1,6] but provide substantial savings in computational time and disk storage.

Density functional theory (DFT) is developing as a cost-effective method for the evaluation of physical properties of molecules. It has been examined for the calculation of geometries and vibrational frequencies of first- and second-row molecules and has been found to give results similar to or better than MP2 theory.[7−9] Some of the functionals (B3LYP and B3PW91) have also been found to give reasonable thermochemical data with an average absolute deviation of about twice that of G2 theory,[6,9] if a large enough basis set is used. In this paper we assess four DFT methods (B3LYP, BLYP, B3PW91, and BPW91) on the 40 energies used to test G2 theory for the third row. A comparison is also made with MP2 theory and experiment for the geometries of the molecules in the test set.

II. Theoretical Methods

The formulation of G2(MP2) and G2(MP2,SVP) theories for the third row is analogous to that of first and second rows.[3,4] The following modifications, which were used in G2 theory for the third row, are incorporated.

1. The MP2 geometry optimizations and the Hartree−Fock vibrational frequency calculations use the 641(d) basis set of Binning and Curtiss[10] for Ga−Kr along with 6-31G(d) for first- and second-row atoms, referred to overall for simplicity as "6-31G(d)". The same scale factor (0.8929) is used for the zero-point energies.
2. The single-point energy calculations use the 6-311G basis and appropriate supplementary functions for first- and second-row atoms and corresponding sets that were developed[2] for Ga−Kr, referred to overall again for simplicity as "6-311G". The single-point energy calculations are done at the QCISD(T)/6-311G(d,p) and MP2/6-311+G(3df,2p) levels in G2(MP2) theory[3] and at the QCISD(T)/6-31G(d) and MP2/6-311+G(3df, 2p) levels in G2(MP2,SVP) theory.[4,5]
3. The splitting factor of the d-polarization functions for the 3df basis set extension is 3 rather than the factor of 4 used for first- and second-row atoms. The 3d core orbitals and 1s virtual orbitals are frozen in the single-point correlation calculations.
4. First-order spin−orbit energy corrections, ΔE(SO), are included in the G2 energies for the third row for ^{2}P and ^{3}P atoms and $^2\Pi$ molecules. Values for these corrections are obtained from spin−orbit configuration interaction calculations.[2,11] The inclusion of first-order atomic and molecular spin−orbit corrections has been found to be important for attaining good agreement with experiment.[2]

Four density functional methods (BPW91, BLYP, B3PW91, and B3LYP) were assessed for the third-row molecules. The BPW91 functional combines the 1988 exchange functional of Becke[12] with the correlation functional of Perdew and Wang.[13] Both components involve local density gradients as well as densities. The Becke part involves a single parameter that fits the exchange functional to accurate computed atomic data. The BLYP functional also uses the Becke 1988 part for exchange, together with the correlation part of Lee, Yang, and Parr.[14] This LYP functional is based on a treatment of the helium atom and really only treats correlation between electrons of opposite spin. A number of other functionals use parameters that are fitted to

---

[†] 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.

⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

S1089-5639(97)01491-6 CCC: $14.00

TABLE 1: Equilibrium Geometries from Density Functional Theory[a]

			geometry					
molecule	symmetry	parameter	MP2	B3LYP	BLYP	B3PW91	BPW91	expt[b]
GeH_4 ($^1A_1$)	T_d	R	1.542	1.541	1.549	1.536	1.544	1.514
AsH ($^3\Sigma^-$)	$C_{\infty v}$	R	1.546	1.555	1.567	1.547	1.560	1.535
AsH^+ ($^2\Pi$)	$C_{\infty v}$	R	1.545	1.556	1.568	1.548	1.561	
AsH_2 ($^2B_1$)	C_{2v}	R	1.539	1.555	1.561	1.542	1.555	1.518
		A	91.1	90.1	89.8	90.1	89.7	90.7
AsH_2^+ ($^1A_1$)	C_{2v}	R	1.539	1.556	1.563	1.543	1.556	
		A	91.6	90.3	90.0	90.4	89.9	
AsH_3 ($^1A_1$)	C_{3v}	R	1.536	1.545	1.557	1.538	1.551	1.511
		A	91.8	90.8	90.2	90.7	90.1	92.1
SeH ($^2\Pi$)	$C_{\infty v}$	R	1.486	1.496	1.506	1.488	1.499	1.475
SeH^+ ($^3\Sigma^-$)	$C_{\infty v}$	R	1.502	1.512	1.522	1.502	1.514	
SeH^- ($^1\Sigma^+$)	$C_{\infty v}$	R	1.491	1.505	1.514	1.496	1.508	
SeH_2 ($^1A_1$)	C_{2v}	R	1.48	1.485	1.500	1.482	1.493	1.46
		A	91.2	90.5	90.2	90.5	90.1	90.6
SeH_2^+ ($^2B_1$)	C_{2v}	R	1.495	1.505	1.515	1.496	1.508	
		A	91.9	91.1	90.7	91.1	90.6	
HBr ($^1\Sigma^+$)	$C_{\infty v}$	R	1.435	1.437	1.452	1.435	1.446	1.414
HBr^+ ($^2\Pi$)	$C_{\infty v}$	R	1.467	1.473	1.485	1.466	1.477	1.448
As_2 ($^1\Sigma^+{}_g$)	$D_{\infty h}$	R	2.142	2.095	2.127	2.086	2.110	2.103
BBr ($^1\Sigma^+$)	$C_{\infty v}$	R	1.893	1.913	1.929	1.903	1.919	1.888
Br_2 ($^1\Sigma^+{}_g$)	$D_{\infty h}$	R	2.308	2.318	2.351	2.298	2.319	2.281
Br_2^+ ($^2\Pi_g$)	$D_{\infty h}$	R	2.235	2.238	2.271	2.215	2.242	
BrCl ($^1\Sigma^+$)	$C_{\infty v}$	R	2.165	2.186	2.214	2.163	2.184	2.136
BrF ($^1\Sigma^+$)	$C_{\infty v}$	R	1.784	1.789	1.813	1.775	1.798	1.759
BrF^+ ($^2\Pi$)	$C_{\infty v}$	R	1.699	1.702	1.740	1.701	1.727	
NaBr ($^1\Sigma^+$)	$C_{\infty v}$	R	2.514	2.476	2.499	2.491	2.503	2.502
$NaBr^+$ ($^2\Pi$)	$C_{\infty v}$	R	2.901	2.856	2.875	2.892	2.911	
BrO ($^2\Pi$)	$C_{\infty v}$	R	1.750	1.757	1.785	1.747	1.765	1.717
BrO^- ($^1\Sigma^+$)	$C_{\infty v}$	R	1.836	1.875	1.900	1.851	1.869	1.814
HOBr ($^1A'$)	C_s	R_{OBr}	1.863	1.867	1.902	1.852	1.880	1.834
		R_{OH}	0.979	0.974	0.987	0.972	0.983	0.961
		A	101.6	101.8	100.8	102.1	100.9	102.3
$HOBr^+$ ($^2A''$)	C_s	R_{OBr}	1.723	1.757	1.800	1.747	1.781	
		R_{OH}	1.003	0.994	1.007	0.992	1.004	
		A	110.1	108.8	107.5	108.8	107.6	
GaCl ($^1\Sigma^+$)	$C_{\infty v}$	R	2.218	2.248	2.271	2.234	2.250	2.202
GeO ($^1\Sigma^+$)	$C_{\infty v}$	R	1.667	1.647	1.671	1.642	1.664	1.625
GeS_2 ($^1\Sigma^+{}_g$)	$D_{\infty h}$	R	2.008	2.016	2.040	2.004	2.022	
H_3CBr ($^1A_1$)	C_{3v}	R_{HC}	1.087	1.089	1.095	1.089	1.095	1.082
		R_{BrC}	1.948	1.960	1.990	1.948	1.965	1.934
		A(HCH)	111.1	111.1	111.4	111.0	111.1	111.2
H_4CBr^+ ($^1A'$)	C_s[c]	R_{CBr}	2.003	2.034	2.066	2.004	2.024	
		R_{BrH1}	1.452	1.458	1.469	1.451	1.462	
		R_{CH2}	1.088	1.090	1.097	1.090	1.097	
		R_{CH3}	1.086	1.088	1.094	1.088	1.095	
		A(H1BrC)	97.3	97.5	96.8	97.1	96.9	
		A(H2CBr)	102.7	101.9	101.6	102.5	102.2	
		A(H3CBr)	105.8	105.3	104.8	105.8	105.6	
		A(H4CH3)	115	115.6	115.9	115.2	115.5	
KrF_2 ($^1\Sigma^+{}_g$)	$D_{\infty h}$	R	1.917	1.933	1.964	1.903	1.943	1.875

[a] The 6-31G(d) basis set is used. Bond angles in degrees, bond lengths in angstroms, MP2/6-31G(d) results from ref 2. [b] References for experiment are given in ref 2. [c] H1 is attached to Br, H2 is trans to H1, and H3 and H4 are equivalent.

energies in the original G2 test set of energies of systems containing first- and second-row elements.[1] These give a functional that is a linear combination of Hartree−Fock exchange, 1988 Becke exchange, and various correlation parts. This idea was introduced by Becke,[15] who obtained parameters by fitting to the molecular data. This is the basis of the B3PW91 functional. The B3LYP functional is constructed in a similar manner, although the parameters are the same as in B3PW91.

The DFT energies are calculated using the 6-311+G(3df, 2p) basis set[2] at the MP2(full)/6-31G(d) geometries reported previously.[2] Scaled HF/6-31G(d) zero-point energies and spin−orbit corrections from ref 2 are added to the density functional energies for calculation of reaction energies. We also calculated geometries of the molecules with the four DFT methods using the 6-31G(d) basis set for comparison with experiment. All of the DFT calculations as well as those for the G2 methods were done with the Gaussian 94 computer program.[16]

TABLE 2: Average Absolute Deviations for Bond Angles and Bond Lengths[a]

method	bond lengths	bond angles
B3LYP	0.030	0.53
BLYP	0.048	0.95
B3PW91	0.020	0.48
BPW91	0.034	1.00
MP2	0.022	0.42

[a] Average absolute deviations with experiment of geometries in Table 1. Bond lengths in angstroms, bond angles in degrees.

III. Results and Discussion

A. Geometries. The optimized geometries from the density functional theories are listed in Table 1, and the corresponding average absolute deviations from experiment are given in Table

TABLE 3: G2(MP2) and G2(MP2,SVP) Energies (Hartrees)

species	G2(MP2)	G2(MP2,SVP)	species	G2(MP2)	G2(MP2,SVP)
Ga	−1923.240 93	−1923.241 73	SeH_2	−2401.165 67	−2401.164 81
Ga^+	−1923.023 07	−1923.024 47	SeH_2^+	−2400.805 04	−2400.804 12
Ge	−2075.359 94	−2075.360 40	HBr	−2573.166 46	−2573.165 85
Ge^+	−2075.073 73	−2075.074 20	HBr^+	−2572.742 43	−2572.741 56
Ge^-	−2075.403 01	−2075.403 10	GeO	−2150.591 58	−2150.591 36
As	−2234.250 29	−2234.250 30	GeS_2	−2870.966 23	−2870.968 15
As^+	−2233.895 25	−2233.895 43	As_2	−4468.643 14	−4468.643 93
Se	−2399.923 68	−2399.923 30	BrCl	−3032.277 84	−3032.278 61
Se^+	−2399.572 93	−2399.572 72	BrF	−2672.252 99	−2672.253 29
Br	−2572.529 09	−2572.528 91	BrF^+	−2671.825 05	−2671.824 11
Br^+	−2572.101 18	−2572.100 48	BrO	−2647.593 59	−2647.594 26
Br^-	−2572.650 16	−2572.649 49	BrO^-	−2647.683 48	−2647.683 72
Kr	−2752.172 63	−2752.172 06	HOBr	−2648.249 46	−2648.249 00
Kr^+	−2751.664 95	−2751.662 52	$HOBr^+$	−2647.859 75	−2647.859 48
GeH_4	−2077.796 97	−2077.794 43	BBr	−2597.293 90	−2597.293 34
AsH	−2234.849 70	−2234.849 30	NaBr	−2734.512 41	−2734.512 12
AsH^+	−2234.500 44	−2234.500 25	$NaBr^+$	−2734.204 04	−2734.203 98
AsH_2	−2235.458 44	−2235.457 61	Br_2	−5145.127 91	−5145.127 15
AsH_2^+	−2235.116 56	−2235.116 00	Br_2^+	−5144.744 09	−5144.746 72
AsH_3	−2236.075 84	−2236.074 58	CH_3Br	−2612.382 62	−2612.380 76
SeH	−2400.541 50	−2400.540 88	CH_4Br^+	−2612.634 94	−2612.632 65
SeH^+	−2400.183 57	−2400.182 97	GaCl	−2383.084 75	−2383.086 52
SeH^-	−2400.621 22	−2400.620 65	KrF_2	−2951.468 47	−2951.467 94

TABLE 4: Deviation of Calculated Atomization Energies (ΣD) from Experiment (kcal/mol)[a]

species	expt[b]	G2(MP2)	G2(MP2,SVP)	B3LYP	BLYP	B3PW91	BPW91
GeH_4	270.5	3.4	1.9	2.8	−2.8	−0.4	−6.3
AsH	64.6	−2.2	−2.5	3.0	3.2	0.6	0.2
AsH_2	131.1	−0.5	−1.0	6.2	5.9	2.0	1.0
AsH_3	206.0	−1.7	−2.5	4.0	3.0	−1.2	−2.9
SeH	74.3	−0.1	−0.5	1.6	1.5	0.5	0.4
SeH_2	153.2	−1.1	−1.7	−1.1	−1.7	−2.4	−3.1
HBr	86.5	−0.2	−0.6	−1.8	−2.2	−1.6	−1.8
GaCl	109.9	0.7	1.3	−2.1	−2.1	−0.7	0.2
GeO	155.2	3.2	2.2	−3.0	8.0	−5.7	5.6
As_2	91.3	−1.9	−1.4	1.1	9.4	−4.4	3.2
BrCl	51.5	0.1	0.0	−3.2	−0.6	−0.5	3.2
BrF	58.9	0.8	0.3	−2.7	3.9	−2.5	4.7
BrO	55.3	−1.3	−1.8	1.6	11.3	2.0	12.5
Br_2	45.4	−1.4	−1.9	−4.0	−1.6	−1.5	2.0
BBr	103.5	−1.7	−1.3	−6.2	−4.4	−3.5	−0.6
NaBr	86.2	0.0	−0.2	−5.4	−6.9	−4.4	−5.5
CH_3Br	358.2	−0.6	−0.8	−2.5	−5.8	−0.5	−1.9
GeS_2	191.7	4.0	4.5	−6.0	−2.0	−0.5	5.9
KrF_2	21.9	2.3	0.6	4.6	24.2	4.3	24.7

[a] Density functional results calculated with the 6-311+G(3df,2p) basis at MP2(full)/6-31G(d) geometries. Spin−orbit corrections and scaled HF/6-31G(d) zero-point energies from ref 2 are included in the DFT energies. [b] See ref 2 for experimental references.

2. The B3PW91 method gives the best agreement with experiment, having an average absolute deviation from experiment of 0.020 Å for bond lengths and 0.48° for bond angles. This is about the same as MP2/6-31G(d), which is 0.022 Å for bond lengths and 0.42° for bond angles. The range of the B3PW91 deviations for bond lengths is 0.037 to −0.017 Å, with the maximum deviation (0.037 Å) occurring for BrO^-. The B3PW91/6-31G(d) bond lengths are all longer than experiment with the exception of two molecules, As_2 and NaBr. This is similar to MP2/6-31G(d) which overestimates all of the bond lengths. The B3PW91 bond angle deviations range from −0.1° to −1.4°, with the maximum deviation (−1.4°) occurring for AsH_3.

The B3LYP/6-31G(d) method has an average absolute deviation from experiment of 0.030 Å and 0.53° for bond lengths and bond angles, respectively. The deviations range from 0.061 to −0.026 Å for bond lengths and from −0.1° to −1.3° for bond angles. For bond lengths the other two methods, BLYP and BPW91, have average absolute deviations from experiment of 0.048 and 0.034 Å, respectively. The bond length deviations range from 0.089 to −0.003 Å for BLYP and 0.068 to 0.001 Å for BPW91. For bond lengths the BLYP and BPW91 functionals have average absolute deviations from experiment of 0.95° and 1.00°, respectively, for bond angles. The bond angle deviations range from 0.2° to −1.9° for BLYP and from −0.1° to −2.0° for BPW91.

B. Energies. The G2(MP2) and G2(MP2,SVP) energies at 0 K (E_0) are listed in Table 3. First-order spin−orbit corrections from ref 2 are included in the energies. The atomization energies, ionization energies, electron affinities, and proton affinities were calculated from these energies. The deviations from experiment for these quantities are listed in Tables 4 and 5. Also listed in these tables are the deviations from experiment of these energies calculated using the four DFT methods. The average absolute deviations of the various methods for the different types of reactions are summarized in Table 6. The set of test energies were chosen in ref 2 from experimental data believed to be reliable to ±1 kcal/mol, which is adequate to judge the accuracy of these methods. However, it should be noted that, due to the sparsity of data, the test set is smaller than used for the first- and second-row elements.[1,6]

TABLE 5: Deviation of Ionization Potentials (IP), Electron Affinities (EA), and Proton Affinities (PA) from Experiment (kcal/mol)[a]

	species	expt[b]	G2(MP2)	G2(MP2,SVP)	B3LYP	BLYP	B3PW91	BPW91
IP	Ga	138.3	−1.6	−2.0	2.3	−1.2	3.1	2.0
	Ge	182.1	−2.6	−2.6	−0.5	−4.6	1.5	0.3
	As	225.7	−2.9	−3.0	−3.2	−6.6	0.0	−1.8
	Se	224.9	−4.8	−4.9	5.1	1.8	2.7	1.4
	Br	272.4	−3.9	−3.6	2.7	−1.4	1.6	−0.1
	Kr	322.8	−4.3	−3.1	−1.2	−6.4	−1.2	−3.5
	AsH	222.3	−3.2	−3.3	−0.9	−5.6	1.5	−0.4
	AsH_2	217.8	−3.2	−3.4	1.5	−3.0	2.9	1.1
	SeH	227.0	−2.4	−2.4	2.9	−0.8	1.3	−0.1
	SeH_2	228.0	−1.7	−1.6	−0.4	−4.3	−1.0	−2.6
	HBr	268.9	−2.8	−2.6	−1.0	−5.4	−1.3	−3.1
	Br_2	242.6	−1.7	−3.9	−3.8	−10.3	−3.7	−9.1
	HOBr	245.3	−0.8	−0.9	−1.9	−8.1	−2.9	−6.8
	BrF	271.6	−3.1	−2.3	−2.4	−9.2	−3.3	−7.7
	NaBr	191.6	1.9	1.7	6.3	3.1	4.9	3.9
EA	Ge	28.4	−1.4	−1.6	−0.6	−3.4	1.8	1.5
	Br	77.6	−1.6	−1.9	0.7	−2.2	−0.1	−1.0
	BrO	54.4	2.0	1.7	−1.7	−5.9	−3.2	−5.2
	SeH	51.0	−1.0	−1.0	0.6	−1.9	−0.5	−0.9
PA	Br^-	322.6	1.4	1.4	−1.2	−1.4	1.1	1.7
	CH_3Br	157.3	1.1	0.8	1.0	2.5	2.2	3.6

[a] Density functional results calculated with the 6-311+G(3df,2p) basis at MP2(full)/6-31G(d) geometries. Spin–orbit corrections and scaled HF/6-31G(d) zero-point energies from ref 2 are included in the DFT energies. [b] See ref 2 for experimental references.

TABLE 6: Average Absolute Deviations from Experiment (kcal/mol)[a]

property	G2		G2(MP2,SVP)		G2(MP2)		B3LYP		BLYP		B3PW91		BPW91	
ΣD_0	1.24	(5.2)	1.42	(4.5)	1.44	(4.0)	3.32	(6.2)	5.30	(24.2)	2.06	(−5.7)	4.50	(24.7)
EA	0.87	(2.1)	1.57	(−1.9)	1.50	(2.0)	0.92	(−1.7)	3.37	(−5.9)	1.39	(−3.2)	2.15	(−5.2)
IP	1.81	(−3.2)	2.76	(−4.9)	2.72	(−4.8)	2.40	(6.3)	4.79	(−10.3)	2.20	(4.9)	2.92	(−9.1)
PA	0.35	(0.5)	1.10	(1.4)	1.22	(1.4)	1.06	(1.4)	1.98	(2.5)	1.62	(2.2)	2.64	(3.6)
IE, EA, PA	1.48	(−3.2)	2.37	(4.9)	2.35	(4.8)	1.99	(6.3)	4.25	(10.3)	1.99	(4.9)	2.75	(9.1)
total	1.37	(5.2)	1.92	(4.9)	1.92	(4.8)	2.62	(6.3)	4.75	(24.2)	2.03	(5.7)	3.58	(24.7)

[a] Maximum deviation in parentheses.

1. G2(MP2) and G2(MP2,SVP) Theories. The G2(MP2) and G2(MP2,SVP) atomization energies have average absolute deviations from experiment of 1.44 and 1.42 kcal/mol, respectively, compared with 1.24 kcal/mol for G2 theory. Three atomization energies deviate by more than 2.3 kcal/mol (0.1 eV) from experiment at the G2(MP2) level [GeH_4 (3.4), GeO (3.2), and GeS_2 (4.0)], and three deviate by more than 2.3 kcal/mol from experiment at the G2(MP2,SVP) level [AsH (−2.5), AsH_3 (−2.5), and GeS_2 (4.5)]. Two atomization energies deviate by more than 2.3 kcal/mol from experiment at the G2 level [GeH_4 (5.2) and Br_2 (2.4)].[2]

The G2(MP2) and G2(MP2,SVP) ionization energies, electron affinities, and proton affinities have average absolute deviations from experiment of 2.35 and 2.37 kcal/mol, respectively, compared with 1.48 kcal/mol for G2 theory. Ten of these energies, all ionization energies, deviate by more than 2.3 (0.1 eV) kcal/mol from experiment at both the G2(MP2) and G2(MP2,SVP) levels. At both levels the ionization energy of Se has the largest deviation (−4.8 kcal/mol and −4.9 kcal/mol, respectively). Gaussian-2 theory deviates from experiment by more than 2.3 kcal/mol in only two cases, the ionization energies of Se (−2.5) and Kr (−3.2).

2. Density Functional Theory. The DFT atomization energies in Table 4 have average absolute deviations from experiment of 3.32, 5.30, 2.06, and 4.50 kcal/mol for the B3LYP, BLYP, B3PW91, and BPW91 methods, respectively. The B3PW91 functional performs the best of the four DFT methods for atomization energies, although not as good as G2(MP2,SVP) or G2(MP2). Eight B3PW91 atomization energies deviate by more than 2.3 kcal/mol (0.1 eV) from experiment, with a maximum deviation of −5.7 kcal/mol (GeO). Thirteen B3LYP atomization energies deviate by more than 2.3 kcal/mol from experiment, with a maximum deviation for AsH_2 (6.2 kcal/mol). The BLYP and BPW91 atomization energies have maximum deviations of 24.2 and 24.7 kcal/mol, respectively (for KrF_2).

The DFT ionization energies, electron affinities, and proton affinities in Table 5 have average absolute deviations from experiment of 1.99, 4.25, 1.99, and 2.75 kcal/mol for the B3LYP, BLYP, B3PW91, and BPW91 functionals, respectively. The B3PW91 and B3LYP functionals perform the best of the four DFT methods for these energies and are actually slightly better than G2(MP2,SVP) or G2(MP2) theory. The B3PW91 functional does better than B3LYP on ionization energies (2.20 vs 2.40 kcal/mol), but worse than B3LYP on electron affinities (1.39 vs 0.92 kcal/mol) and proton affinities (1.62 vs 1.06 kcal/mol).

The overall average absolute deviation from experiment (for all properties) is 1.92 kcal/mol for both G2(MP2) and G2(MP2,SVP), compared with 1.37 kcal/mol for G2 theory (see Table 6). The B3PW91 method has an overall average absolute deviation of 2.03 kcal/mol. This is almost as good as G2(MP2) and G2(MP2,SVP) theory and is due to the good performance of B3PW91 for dissociation energies and ionization energies. The B3LYP functional has an overall average absolute deviation from experiment of 2.62 kcal/mol, while the pure density functional methods, BLYP and BPW91, have the largest errors, with average absolute deviations of 4.75 and 3.58 kcal/mol, respectively.

IV. Conclusions

The following conclusions can be drawn from this assessment of modified G2 theories and density functional theories for species containing third-row atoms Ga−Kr based on the 40 test energies (atomization energies, ionization energies, and electron affinities used to assess G2 theory).

1. The G2(MP2) and G2(MP2,SVP) theories both have an average absolute deviation of 1.92 kcal/mol from experiment for 40 test energies, compared with 1.37 kcal/mol for G2 theory. While the G2(MP2) and G2(MP2,SVP) results are not as good as the G2 results, the overall average absolute deviations are still within 2 kcal/mol. Since G2(MP2,SVP) is computationally more efficient than G2(MP2), it may be preferable to G2(MP2) for third-row species.

2. For the 40 test energies, the B3PW91 density functional method gives the best overall agreement with experiment of the four DFT methods (average absolute deviation of 2.03 kcal/mol). It does nearly as well as G2(MP2) and G2(MP2, SVP) theories. As in the case of first- and second-row systems, the hybrid DFT methods, B3LYP and B3PW91, do significantly better than the pure DFT methods, BLYP and BPW91. Also B3PW91 does better than B3LYP for reaction energies, in contrast to the first- and second-row systems, where B3LYP performs better.

3. Of the four DFT methods, the B3PW91/6-31G(d) optimized geometries are in the best agreement with experiment, with an accuracy about the same as MP2/6-31G(d). The B3LYP/6-31G(d) method also gives a good account of the geometries with only slightly larger overall deviations.

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Materials Sciences, under Contract No. W-31-109-ENG-38. We acknowledge a grant of computer time at the National Energy Research Supercomputer Center.

References and Notes

(1) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys*. **1991**, *94*, 7221.

(2) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C., Jr.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(3) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys*. **1993**, *98*, 1293.

(4) Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys*. **1996**, *104*, 5148.

(5) Smith B. J.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 6468.

(6) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys*. **1997**, *106*, 1063.

(7) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys*. **1993,** *98*, 5612.

(8) Scott A. P.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 16502.

(9) Bauschlicher, C. W. *Chem. Phys. Lett.* **1995**, *246*, 40.

(10) Binning R. C.; Curtiss L. A. *J. Comput. Chem*. **1990**, *11*, 1206.

(11) Blaudeau J.-P.; Curtiss L. A. *Int. J. Quantum Chem*. **1997**, *61*, 943.

(12) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(13) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewskiv, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.