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Gallium Clusters Ga_n ($n = 1-6$): Structures, Thermochemistry, and Electron Affinities

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Eight different density functional theory (DFT) and hydrid Hartree−Fock/DFT methods have been employed for studying the structures, electron affinities, and dissociation energies of the Ga_n/Ga_n^- ($n = 1-6$) species. The basis set used in this work is of double-ζ plus polarization quality with additional s- and p-type diffuse functions, denoted DZP++. The geometries were fully optimized with each DFT method independently. Located were 22 different structures for the neutral clusters and 15 structures for the anionic clusters, and the results are in broad agreement with the limited experimental results. High-spin electronic states appear to be preferred in the Ga_n clusters when $n < 4$. Triangular and planar rectangular structures are the global minima for Ga_3 and Ga_4, respectively, while the global minima for Ga_5 and Ga_6 are low-spin nonplanar structures. The three types of neutral anion energy separations reported in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). As in previous studies, the HF/DFT hybrid methods predict shorter and more reliable bond lengths than the pure DFT methods, and the BHLYP method appears to be the best for predicting geometries. The BP86 method-predicted VDE values for the anionic gallium clusters are in reasonable agreement with the experimental values. The BP86-predicted EA_{ad} values, which are also considered to be reliable, are 1.51 (Ga_2), 1.81 (Ga_3), 2.14 (Ga_4), 2.27 (Ga_5), and 2.31 eV (Ga_6). The first dissociation energies for the neutral gallium clusters predicted by the B3LYP method are 1.30 (Ga_2), 1.58 (Ga_3), 1.98 (Ga_4), 1.80 (Ga_5), and 2.29 eV (Ga_6). Only the dissociation energy for Ga_2 (1.10 eV) is known from the experiment. The anion dissociation energies are predicted for both the $Ga_{n-1} + Ga^-$ and the $Ga_{n-1}^- + Ga$ dissociation limits. The harmonic vibrational frequencies are also reported. Since most of the structures, bond dissociation energies, and vibrational frequencies for the neutral and anionic gallium clusters are experimentally unknown, it is hoped that this work will stimulate further explorations in the laboratory.

Introduction

Great interest has been focused in recent years on the study of the structure and electronic properties of small metal clusters[1,2] because they are often considered to be the bridges between isolated atoms and bulk matter and they have fascinating chemical and physical properties. The group 13 elements are among the key building blocks for the modern III−V semiconductor diode lasers. The Ga_n clusters are considerably important in the thin-film deposition and for the thin-layer growth in the deposition of multilayer structures. The organometallic icosogen (gallium, indium, and thallium)-containing group 13 clusters, with particular emphasis on gallium, have been studied ebulliently.[3] There are some spectroscopic studies of the gallium dimer Ga_2, including the electronic spectra of Ginter, Ginter, and Innes,[4] Tan and Dagdigian,[5] and Douglas, Hauge, and Margrave.[6] Also reported for Ga_2 are Raman spectra by Froben, Schulze, and Kloss,[7] photoelectron spectroscopy by Cha, Ganteför, and Eberhardt,[8] and Knudsen cell-mass spectra by Balducci, Gigli, and Meloni.[9] There are many previous theoretical studies for the Ga_2 dimer.[10−20] It has been established that Ga_2 has a $^3\Pi_u$ ground state with a low-lying $^3\Sigma_g^-$ excited state,[4,5,7,8,10,14−16,19,20] while Ga_2^- has a $^4\Sigma_g^-$ ground state with a low-lying excited $^2\Sigma_g^-$ state.[8,15−18] Neutral Ga_3 has a $^2A_1$ (C_{2v}) ground state with a low-lying, nearly degenerate $^4A_2$ (C_{2v}) state,[21−24] while the anionic Ga_3^- has a $^1A_1'$ (D_{3h}) ground state.[25] Ga_4 has a planar rhombus structure of D_{2h} symmetry.[22,24,26] The Ga_5 and Ga_6 clusters form three-dimensional structures.[23,24] Although there have been a number of studies of the gallium dimer[14−20] and clusters containing gallium and other elements,[27−31] there are virtually no experimental studies on the larger "naked" gallium clusters.[8]

The theoretical prediction of electron affinities has historically been difficult due to the desired result being a small difference between two large energies, but recent work has shown that the density functional theory (DFT) methods are dependable for EA predictions, while requiring less computational effort than convergent quantum mechanical methods such as the coupled-cluster theory. The application of the gradient-corrected density functional theory has been shown to be effective for many inorganic species.[32−34] For a general discussion of the reliability of DFT studies of anions, the reader is referred to the 2002 review of Rienstra-Kiracofe, Tschumper, Schaefer, Nandi, and Ellison.[35]

The object of the present study is to systematically apply several contemporary forms of the density functional theory to determine the electron affinities and other properties of the Ga_n ($n = 1-6$) clusters. Of specific interest are (a) finding the most stable structure and ground state of the Ga_n ($n = 2-6$) clusters

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TABLE 1: Zero-Point Vibrational Energies (eV) within the Harmonic Approximation for the Global Minima of Ga_n/Ga_n^- ($n = 2-6$)[a]

isomers	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
Ga_2	0.010	0.010	0.009	0.010	0.010	0.010	0.010	0.010
Ga_2^-	0.012	0.013	0.011	0.012	0.013	0.012	0.012	0.013
$\Delta(Ga_2 - Ga_2^-)$	−0.002	−0.002	−0.002	−0.002	−0.002	−0.002	−0.002	−0.003
Ga_3	0.024	0.026	0.023	0.025	0.027	0.026	0.027	0.029
Ga_3^-	0.028	0.029	0.026	0.028	0.030	0.028	0.029	0.032
$\Delta(Ga_3 - Ga_3^-)$	−0.003	−0.007	−0.003	−0.003	−0.003	−0.003	−0.003	−0.003
Ga_4	0.039	0.041	0.039	0.037	0.042	0.039	0.041	0.043
Ga_4^-	0.051	0.050	0.050	0.053	0.053	0.053	0.053	0.057
$\Delta(Ga_4 - Ga_4^-)$	−0.012	−0.009	−0.011	−0.016	−0.012	−0.014	−0.012	−0.014
Ga_5	0.061	0.065	0.059	0.063	0.067	0.064	0.067	0.075
Ga_5^-	0.070	0.073	0.066	0.072	0.075	0.073	0.075	0.080
$\Delta(Ga_5 - Ga_5^-)$	−0.009	−0.009	−0.007	−0.009	−0.008	−0.009	−0.008	−0.004
Ga_6	0.090	0.092	0.085	0.093	0.097	0.094	0.097	0.104
Ga_6^-	0.090	0.091	0.087	0.094	0.097	0.095	0.096	0.106
$\Delta(Ga_6 - Ga_6^-)$	0.000	0.001	−0.002	−0.001	0.000	−0.001	0.001	−0.002

[a] All results were obtained with the DZP++ basis set.

and their anions; (b) establishing the relationship between the neutral Ga_n molecules and their anions as measured by the three types of energy separations, namely, the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy of the anion (VDE); (c) comparing the electron affinities with the limited available experimental results; (d) predicting other properties, including dissociation energies and vibrational frequencies; and (e) comparing the different DFT methods. We would like to establish reliable theoretical predictions for these gallium clusters in the absence of experimental results and in some cases to challenge existing experiments.

Theoretical Methods

The eight independent density functional or hybrid Hartree–Fock density functional forms used here are (a) Becke's 1988 exchange functional[36] with the Lee, Yang, and Parr correlation functional[37] (BLYP), (b) Becke's half-and-half exchange functional[38] with the LYP correlation functional (BHLYP), (c) Becke's hybrid three-parameter functional[39] with the LYP correlation functional (B3LYP), (d) Becke's 1988 exchange functional[36] with the Perdew correlation functional[40] (BP86), (e) Becke's three-parameter hybrid exchange functional[39] with Perdew's correlation functional[40] (B3P86), (f) Becke's 1988 exchange functional[36] with the Perdew–Wang 1991 correlation functional[41] (BPW91), (g) Becke's three-parameter hybrid exchange functional[39] with the Perdew–Wang 1991 correlation functional[41] (B3PW91), and (h) Vosko, Wilk, and Nusair's local correlation functional with Slater's exchange functional[42,43] (LSDA).

The present research used standard double-ζ plus polariztion (DZP) basis sets augmented with diffuse functions, labeled as DZP++. These basis sets have been comprehensively calibrated for the prediction of electron affinities using density functional methods.[35] The DZP++ basis set for gallium was constructed using the Schäfer–Horn–Ahlrichs' standard double-ζ spd set and a set of pure d-type polarization functions, $\alpha_d(Ga) = 0.207$,[44] and then adding a set of sp diffuse functions, $\alpha_s(Ga) = 0.001802$ and $\alpha_p(Ga) = 0.015366$. The diffuse function's orbital exponents were determined in an "even-tempered sense" as a mathematical extension of the primitive set, according to the prescription of Lee and Schaefer.[45] The final contraction scheme for this basis set is Ga(15s12p6d/9s7p3d). The total number of DZP++ contracted Gaussian basis functions ranged from 45 for Ga/Ga^- to 270 for Ga_6/Ga_6^-.

TABLE 2: Electron Affinities (EA) of Atomic Ga (eV)

method	EA	method	EA
B3LYP	0.42	B3P86	0.95
BHLYP	0.23	BPW91	0.47
BLYP	0.38	B3PW91	0.47
BP86	0.59	LSDA	0.98
experiment	0.43 ± 0.03[a]		
	0.45 ± 0.2[b]		
	0.3 ± 0.15[c]		
CIPSI	0.29[d]		

[a] From ref 48. [b] From ref 8. [c] From ref 47. [d] From ref 49.

Spin-restricted methods were used for all closed-shell systems, while spin-unrestricted methods were employed for the open-shell species. The SCF iterative procedures were converged to a threshold of 10^{-8} based on the density. The default numerical integration grid (75 302) was initially applied; however, we also used the finer grid (99 590) to check for suspicious results, and sometimes this finer integration grid was important for the gallium clusters. The computations were performed with the Gaussian 98 program package[46] in Beijing.

All Ga_n and Ga_n^- ($n = 2-6$) stationary points were confirmed to be minima or otherwise by the evaluation of their harmonic vibrational frequencies at each level of theory. The zero-point vibrational energies (ZPVE) evaluated by the eight methods are presented in Table 1. The ZPVE differences between Ga_n and Ga_n^- ($n = 2-6$) are quite small, ranging from 0.001 to 0.016 eV. These differences may be used as a correction to the adiabatic electron affinities.

Results and Discussion

Ga and Ga^-. The experimental electron affinity of the $^2P_{1/2}$ state of the Ga atom was known before 1985 to be 0.3 ± 0.15 eV.[47] Theoretically Arnau et al.[49] predicted the EA to be 0.29 eV from the CIPSI method (configuration interaction by perturbation with multiconfigurational zero-order wave function selected by iterative process) in 1992. A more recent experimental result, 0.45 ± 0.2 eV, was obtained by Cha, Ganteför, and Eberhardt[8] from photoelectron spectroscopy in 1994. The most accurate current value, 0.43 ± 0.03 eV, was derived by Williams et al.[48] using laser photodetachment electron spectrometry in 1998. Our present DFT EA values with various functionals are listed in Table 2 and are compared with the experimental[8,47,48] and earlier theoretical studies.[49] The EA values predicted by the BLYP (0.38 eV), B3LYP (0.42 eV), BPW91 (0.47 eV), B3PW91 (0.47 eV), and BP86 (0.59 eV) methods are fairly close to the most accurate experimental value (0.43 ± 0.03 eV).[48] The BHLYP method predicts an EA that is too low (0.23 eV), while the B3P86 and LSDA methods predict EA values that are too high (0.95 and 0.98 eV, respectively).

TABLE 3: Bond Distances r_e (Å) and Vibrational Frequencies ω_e (cm^{-1}) for the Low-Lying States of Neutral and Charged Gallium Dimers[a]

state	method	r_e	ω_e
Ga_2 **2a** X $^3\Pi_u$	B3LYP	2.749	156
	BHLYP	2.712	167
	BLYP	2.795	145
	BP86	2.743	155
	B3P86	2.702	156
	BPW91	2.740	165
	B3PW91	2.712	163
	LSDA	2.651	167
	SOCI[b]	2.746	162
	FOCI[b,c]	2.762	158
	CI[d]	2.730	172
	CASSCF[d]	2.719	174
	MRD-CI[e]	2.772	158
	MRD-CI[f]	2.748	162
	MRSDCI[g]	2.685	170
	MRCPA(4)[g]	2.693	170
	DF[h]	2.573	184
	experiment[i]		180
2b A $^3\Sigma_g^-$	B3LYP	2.488	199
	BHLYP	2.479	205
	BLYP	2.513	190
	BP86	2.466	207
	B3P86	2.446	214
	BPW91	2.463	208
	B3PW91	2.454	213
	LSDA	2.390	227
	SOCI[b]	2.498	198
	FOCI[b,c]	2.506	197
	CI[d]	2.481	215
	CASSCF[d]	2.460	223
	MRD-CI[e]	2.529	197
	MRD-CI[f]	2.494	197
	MRSDCI[g]	2.448	210
	MRCPA(4)[g]	2.470	210
	DF[h]	2.352	217
2c a $^1\Sigma_g^+$	B3LYP	3.056	133
	BHLYP	3.003	140
	BLYP	3.113	124
	BP86	3.065	130
	B3P86	3.010	137
	BPW91	3.060	130
	B3PW91	3.019	136
	LSDA	2.976	137
	SOCI[b]	3.020	156
	FOCI[b,c]	2.954	129
	CI[d]	3.047	131
	CASSCF[d]	3.021	136
	MRD-CI[f]	3.074	118
	MRSDCI[g]	2.963	125
	MRCPA(4)[g]	2.940	118
2d $^5\Sigma_u^-$	B3LYP	2.311	297
	BHLYP	2.288	317
	BLYP	2.341	275
	BP86	2.317	288
	B3P86	2.289	309
	BPW91	2.315	291
	B3PW91	2.294	307
	LSDA	2.270	309
	DF[h]	2.193	308

[a] The previous theoretical and experimental results are also listed for comparison. [b] From ref 15. [c] From ref 14. [d] From ref 10. [e] From ref 18. [f] From ref 19. [g] From ref 20. [h] From ref 24. [i] From ref 7.

TABLE 4: Bond Distances r_e (Å) and Vibrational Frequencies ω_e (cm^{-1}) for the Low-Lying States of the Anionic Gallium Dimers[a]

state	method	r_e	ω_e
Ga_2^- **2a$^-$** X $^4\Sigma_g^-$	B3LYP	2.560	189
	BHLYP	2.532	203
	BLYP	2.600	172
	BP86	2.552	189
	B3P86	2.518	204
	BPW91	2.552	190
	B3PW91	2.529	201
	LSDA	2.475	210
	SOCI[b]	2.562	197
	FOCI[b]	2.580	191
	MRD-CI[c]	2.661	171
	DF[d]	2.382	215
	MRSDCI[e]	2.517	
	B3LYP[e]	2.545	
	B3PW91[e]	2.520	

[a] The previous theoretical results are also listed for comparison. [b] From ref 15. [c] From ref 18. [d] From ref 23. [e] From ref 17.

TABLE 5: Relative Energies (kcal/mol) for the Ga_2 Diatomic Systems

	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
2a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2b	3.6	5.7	2.7	1.4	2.6	1.6	2.8	−1.1
2c	8.4	8.4	8.5	10.5	10.6	11.1	10.7	10.5
2d	68.0	62.5	72.9	64.4	60.3	61.1	58.2	64.0

Ga_2 and Ga_2^-. In 1965, Ginter, Ginter, and Innes[4] first reported the electronic spectra for Ga_2 in the wavenumber range of 18200−21700 cm^{-1}. Douglas, Hauge, and Margrave[6] reported electronic absorption spectra in 1983 and suggested a $^1\Sigma_g^+$ ground state. In their 1983 Raman spectroscopy study, Froben, Schulze, and Kloss[7] reported a vibrational frequency of 180 cm^{-1} for the Ga_2 ground state. Some mass spectrometric thermochemical studies have determined the gallium dimer dissociation energy,[9−13] and an upper limit for the dissociation energy, D_e < 1.102 eV, was deduced recently by Tan and Dagdigian[5] from electronic spectra.

The present theoretical equilibrium distances r_e (Å) and the vibrational frequencies ω_e (cm^{-1}) for the low-lying states of neutral Ga_2 are given in Table 3, and those for the anionic Ga_2^- may be found in Table 4. The previous theoretical and experimental results are also listed in Tables 3 and 4 for comparison. Since the ground state of the Ga atom has a ^2P symmetry from the $4s^24p$ configuration, the gallium clusters often have several low-lying electronic states. Predicted here are four low-lying states for the neutral Ga_2 dimer: $^3\Pi_u$, $^3\Sigma_g^-$, $^1\Sigma_g^+$, and $^5\Sigma_u^-$. The relative energies (kcal/mol) for these four states of Ga_2 with respect to the ground state are listed in Table 5. The $^3\Pi_u$ state is predicted to be the ground state, which is in agreement with the previous experimental[4,5,7,8] and theoretical[10,14−16,19,20] studies. The $^3\Pi_u$ and $^3\Sigma_g^-$ states are nearly degenerate, as observed for the Al dimer.[16] The $^3\Sigma_g^-$ energy is higher than that of $^3\Pi_u$ by only 1.4−5.7 kcal/mol with seven of the DFT methods, excluding the less-reliable LSDA method, which predicts the $^3\Sigma_g^-$ state to be lower by 1.1 kcal/mol.

The DFT Ga−Ga bond length for the $^3\Pi_u$ ground state is predicted to be 2.712 Å (BHLYP). To our knowledge, there is no experimental bond length for the Ga_2 dimer. The present DFT results are broadly consistent with the previous theoretical studies (see Table 3), except for the 1993 value (2.573 Å) of Jones.[24] The experimental Ga−Ga bond distance in the α-Ga crystal is 2.566 Å,[23] and that for hexagonal β-GaS is 2.444 Å.[50] Similar bond lengths are found in $[Ga_2Cl_6]^{2-}$ (2.39 Å) and

$[Ga_2Br_6]^{2-}$ (2.41 Å).[51] Our predicted Ga−Ga bond length for the Ga dimer in its $^3\Pi_u$ state (**2a**) is somewhat longer than these indirectly related experimental values, while the bond length (2.479 Å, BHLYP) for the $^3\Sigma_g^-$ state (**2b**) is closer to the Ga−Ga condensed-phase bond distances.

The diatomic Ga_2^- radical anion was generated in 2001 by the pulsed-laser vaporization gallium metal and trapped in neon matrices. The ESR results of Stowe and co-workers[17] provide direct experimental evidence that the ground electronic state for Ga_2^- has a $^4\Sigma_g^-$ symmetry. This finding agrees with the photoelectron spectroscopy (PES)[8] and theoretical results.[15,16,18] In the present paper, we have investigated the quartet ($^4\Sigma_g^-$) state for the anionic Ga_2^-. The predicted bond length of the $^4\Sigma_g^-$ state is 2.523 Å (BHLYP), which is shorter than that in the neutral ground state by roughly 0.18 Å, indicating some multiple Ga−Ga bonding character in the anion. This is consistent with the fact that the "last" electron in Ga_2^- occupies a π_u-bonding molecular orbital. This prediction also comports with the higher vibrational frequency for the Ga_2^- anion and the larger dissociation energy of Ga_2^-. A similar trend was observed for anionic $[R_2Ga{-}GaR_2]^-$, R = CHSi(Me)$_3$; the Ga−Ga bond distance (2.401 Å)[52] is shorter than that (2.541 Å)[53] of its neutral analogues by 0.14 Å. A comparable pattern was also reported for $R'_2Ga{-}GaR'_2$ ($R' = 2,4,6\text{-}{}^iPr_3C_6H_3$);[54] for the anion, r(Ga−Ga) is 2.343 Å, and for the neutral, r(Ga−Ga) is 2.515 Å. The lowest excited state has a $^2\Sigma_g^-$ symmetry,[18] and the DFT methods using the Gaussian program may attempt to describe this state with the single determinant [... $8\sigma_g\beta\ 4\pi_{ux}\alpha\ 4\pi_{uy}\alpha$]. However, this single Slater determinant is merely one part of the $^2\Sigma_g^-$-restricted Hartree−Fock wave function, which should be correct as described by a linear combination of Slater determinants. In terms of complex orbitals, the $M_s = +^1/_2$ component of the $^2\Sigma_g^-$ electronic state is

$$\begin{aligned}(\surd 6)^{-1}\,[2 \times 8\sigma_g\beta\ 4\pi_{u+}\alpha\ 4\pi_{u-}\alpha]\\ -8\sigma_g\alpha\ 4\pi_{u+}\beta\ 4\pi_{u-}\alpha\\ -8\sigma_g\alpha\ 4\pi_{u+}\alpha\ 4\pi_{u-}\beta]\end{aligned}$$

and only multiconfiguration methods may be adopted to reasonably treat this state.

Our theoretical neutral anion energy separations for Ga_2, as well as the experimental electron affinity data, are given in Table 6. The zero-point vibrational energy (ZPVE) correction for Ga_2/Ga_2^- is very small, 0.002−0.003 eV (Table 1). The vertical detachment energy (VDE) is predicted to be 1.67 (B3LYP), 1.38 (BHLYP), 1.25 (BLYP), 1.63 (BP86), 2.02 (B3P86), 1.51 (BPW91), 1.50 (B3PW91), and 2.01 eV (LSDA). Some of these predictions (BP86, B3LYP, BPW91, and B3PW91) agree with the literature value of 1.6 ± 0.1 eV[8] within the stated error bars, with the BP86 and B3LYP values (not surprisingly[35]) being the closest. The BLYP and BHLYP methods predict VDE values that are too small, while the B3P86 and LSDA methods overshoot the laboratory VDE values. We will not make further reference to the latter three methods. The range of adiabatic electron [$8\sigma_g\beta\ 4\pi_{ux}a\ 4\pi_{uy}\alpha$] affinities (EA$_{ad}$) for Ga_2 is 1.16−1.51 eV. Excluding the three unreasonable values (predicted by the BHLYP, LSDA, and B3P86 methods), we found that the other five values are close to Balasubramanian's EA(Ga_2) = 1.2 ± 0.2 eV predicted at the second-order CI level of theory.[15] The theoretical vertical electron affinities (EA$_{vert}$) range from 1.10 to 1.45 eV (excluding the same three methods). The values of EA$_{ad}$, EA$_{vert}$, and VDE are close to each other due to the small difference in geometry between the neutral and its anion. The Ga_2^- anion is quite stable due to the substantial VDE value.

TABLE 6: Adiabatic and Vertical Electron Affinities of the Neutral Ga$_n$ (n = 2−5) Clusters and Vertical Detachment Energies of Their Anions [eV (kcal/mol)]

compound	method	EA$_{ad}$	EA$_{vert}$	VDE
Ga_2	B3LYP	1.29 (29.8)	1.23 (28.3)	1.67 (38.6)
	BHLYP	1.13 (26.0)	1.06 (24.4)	1.38 (31.8)
	BLYP	1.16 (26.7)	1.10 (25.3)	1.25 (28.7)
	BP86	1.51 (34.8)	1.45 (33.3)	1.63 (37.5)
	B3P86	1.93 (44.6)	1.86 (43.0)	2.02 (46.5)
	BPW91	1.39 (32.1)	1.33 (30.7)	1.51 (34.7)
	B3PW91	1.42 (32.7)	1.35 (31.1)	1.50 (34.5)
	LSDA	2.02 (46.5)	1.95 (44.9)	2.01 (46.4)
	experiment			1.6 ± 0.1[a]
Ga_3	B3LYP	1.68 (38.8)	1.32 (30.4)	2.28 (52.5)
	BHLYP	1.46 (33.8)	1.13 (35.5)	2.72 (62.7)
	BLYP	1.56 (36.0)	1.16 (26.7)	1.94 (44.7)
	BP86	1.81 (41.7)	1.45 (33.4)	2.16 (49.8)
	B3P86	2.20 (50.8)	1.87 (43.1)	2.79 (64.4)
	BPW91	1.60 (37.0)	1.26 (29.1)	1.95 (44.9)
	B3PW91	1.63 (37.5)	1.30 (30.1)	1.96 (45.1)
	LSDA	2.58 (59.5)	2.22 (51.3)	2.92 (67.3)
	experiment			1.95 ± 0.1[a]
Ga_4	B3LYP	1.95 (45.0)	1.93 (44.6)	2.02 (46.6)
	BHLYP	1.76 (40.6)	1.70 (39.1)	1.83 (42.2)
	BLYP	1.82 (42.1)	1.77 (40.7)	1.90 (43.8)
	BP86	2.14 (49.5)	2.06 (47.4)	2.23 (51.3)
	B3P86	2.56 (59.0)	2.52 (58.1)	2.63 (60.7)
	BPW91	1.99 (45.9)	1.90 (43.9)	2.07 (47.7)
	B3PW91	2.01 (46.3)	1.98 (45.6)	2.08 (48.0)
	LSDA	2.80 (64.6)	2.71 (62.6)	2.89 (66.6)
	experiment			2.40 ± 0.1[a]
Ga_5	B3LYP	2.12 (48.8)	2.07 (47.7)	2.17 (50.1)
	BHLYP	1.98 (40.0)	1.73 (40.0)	2.06 (47.4)
	BLYP	1.96 (45.2)	1.91 (44.1)	2.03 (46.7)
	BP86	2.27 (52.4)	2.23 (51.4)	2.32 (53.4)
	B3P86	2.73 (62.9)	2.65 (61.2)	2.77 (63.9)
	BPW91	2.13 (49.2)	2.09 (48.3)	2.17 (50.0)
	B3PW91	2.18 (50.3)	2.09 (48.1)	2.23 (51.4)
	LSDA	2.80 (64.6)	2.57 (59.3)	2.85 (65.7)
	experiment			2.45 ± 0.1[a]
Ga_6	B3LYP	2.12 (49.0)	1.84 (42.5)	2.38 (54.9)
	BHLYP	2.08 (47.9)	1.81 (41.9)	2.31 (53.3)
	BLYP	1.87 (43.2)	1.56 (36.1)	2.12 (48.8)
	BP86	2.31 (53.2)	2.02 (46.7)	2.53 (58.4)
	B3P86	2.84 (65.4)	2.57 (59.3)	3.08 (71.1)
	BPW91	2.19 (50.4)	1.91 (44.1)	2.41 (55.5)
	B3PW91	2.30 (53.0)	2.04 (47.1)	2.54 (58.6)
	LSDA	2.89 (66.6)	2.63 (60.5)	3.10 (71.5)
	experiment			2.60 ± 0.1[a]

[a] From ref 8.

Ga_3 and Ga_3^-. The predicted geometries of the ground state of Ga_3 and its anion are displayed in Figures 2 and 3, respectively. Linear, isosceles, and equilateral trimers are the three structures to be considered here. There are some previous theoretical studies for Ga_3. Balasubramanian and Feng[21] predicted an isosceles (r = 2.58 Å, α = 61.2°) $^2A_1$ ground state and three low-lying excited states, $^4A_2$, $^2B_1$, and $^4B_1$ within ~0.3 eV of the ground state. Katircioğlu and Erkoç,[22] using molecular dynamics, suggested that the equilateral triangle structure (D_{3h} symmetry, r = 2.54 Å) is the global minimum. Meier, Peyerimhoff, and Grein[18] favored the nearly degenerate $^4A_2$ or $^4B_1$ states and predicted bond lengths significantly (0.1−0.2 Å) longer than those of Balasubramanian and Feng.[21] Gong and Tosatti[23] predicted the isosceles triangle to be more stable than the chain and equilateral triangle structures. Jones[24] predicted the $^2A_1$ state (r = 2.32 Å, α = 60°) to lie ~0.38 eV below the $^2B_1$ (2.44 Å, 60°) and $^4A_2$ (2.41 Å, 74°) states, using a

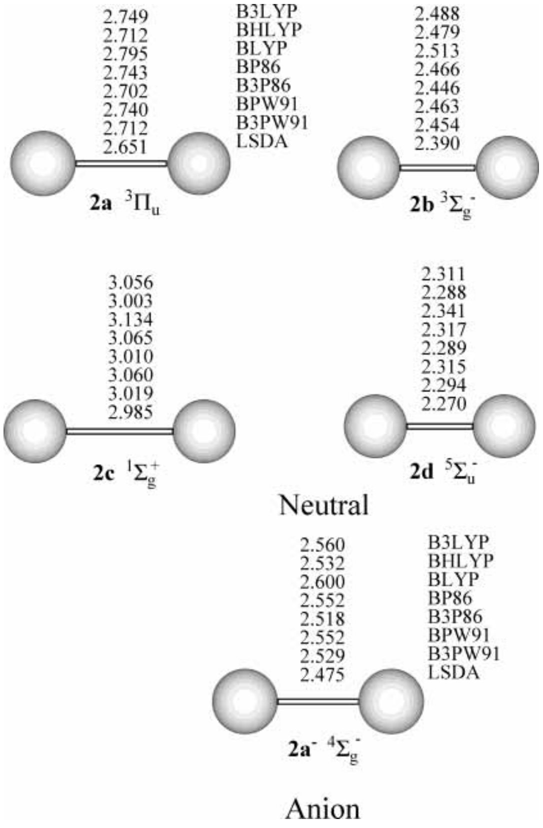


Figure 1. Molecular geometries for the neutral Ga_2 and anionic Ga_2^-. All bond distances are in Å.

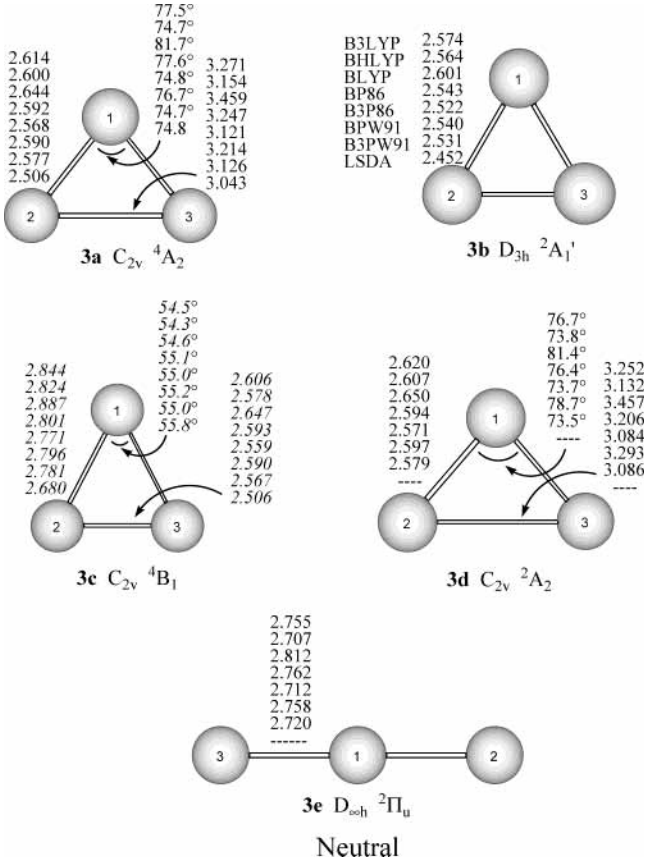


Figure 2. Molecular geometries for neutral Ga_3. All bond distances are in Å. Italic fonts for structure **3c** indicate that it is a transition state.

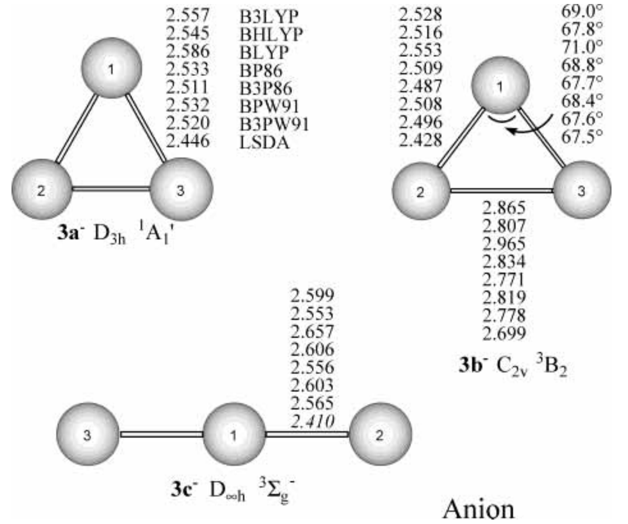


Figure 3. Molecular geometries for anionic Ga_3^-. All bond distances are in Å. Italic fonts for structure **3c**⁻ indicate that it is a transition state.

TABLE 7: Relative Energies (kcal/mol) for the Structures of the Ga_3 Cluster[a]

	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
3a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3b	0.1	1.7	−0.3	−0.4	0.4	0.6	1.2	−6.3
3c	*2.1*	*1.4*	*3.0*	*2.6*	*2.0*	*2.5*	*1.9*	*2.5*
3d	4.0	1.7	4.3	5.9	5.0	6.5	4.5	*b*
3e	8.7	8.2	7.9	12.3	12.7	12.9	12.7	*b*
3a⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3b⁻	4.7	3.1	5.4	4.3	3.3	3.4	2.8	7.6
3c⁻	10.8	9.2	10.2	12.0	11.9	11.0	10.9	*19.1*

[a] Italics indicate the levels of theory at which structure **3c** or **3c**⁻ is a transition state. [b] Not a stationary point.

combination of the density functional (DF) theory with finite-temperature molecular dynamics (MD). The latter paper also predicted a linear equilibrium structure ($^2\Pi_u$ state, $r = 2.41$ Å) lying 0.9 eV above the ground state.

In the present study, the quartet $^4A_2$ state with an isosceles triangular structure (C_{2v} symmetry), **3a**, is predicted to be the global minimum. The quartet D_{3h} symmetry structure has a singly occupied e orbital with the valence electron configuration $(1a_1')^2(1e')^4(1a_2')(2a_1')(2e')$, and it undergoes a Jahn−Teller distortion to C_{2v} symmetry with the $^4A_2$ and $^4B_1$ components. The $^4A_2$ state has the lower energy of the two. The $^4B_1$ structure (**3c**) is a transition state with an imaginary vibrational frequency in all eight DFT methods, lying above **3a** by 1−3 kcal/mol (Table 7). The imaginary vibrational frequency mode leads to a C_s symmetry structure, which eventually collapses to structure **3a**. The fact that the quartet state is the ground state is similar to the case of the Al_3 cluster.[55] The doublet C_{2v} structure predicted by Balasubramanian and Feng[21] leads to an equilateral structure **3b** (D_{3h} symmetry in its $^2A_1'$ state). The DFT methods suggest that structure **3b** lies higher than **3a** with five (B3LYP, BHLYP, B3P86, BPW91, and B3PW91) methods but lies lower with the other three (BLYP, BP86, and LSDA) methods (Table 7). Either way, the energy differences between **3a** and **3b** are less than 2 kcal/mol (except for LSDA); therefore, the two electronic states should be viewed as nearly degenerate. The $^2A_2$ state with C_{2v} symmetry (**3d**) has a longer unique Ga−Ga bond distance. A linear structure **3e** ($^2\Pi_u$ state with electron configuration $\cdots 11\sigma_g^2\ 9\sigma_u^2\ 12\sigma_g^2\ 10\sigma_u^2\ 6\pi_u$) is a minimum predicted by all eight DFT methods. It lies energetically above **3a** by 8−13 kcal/mol. The bond length for **3e** is 2.707 Å (BHLYP), which is obviously longer than that reported in Jones' work (2.41 Å).[24]

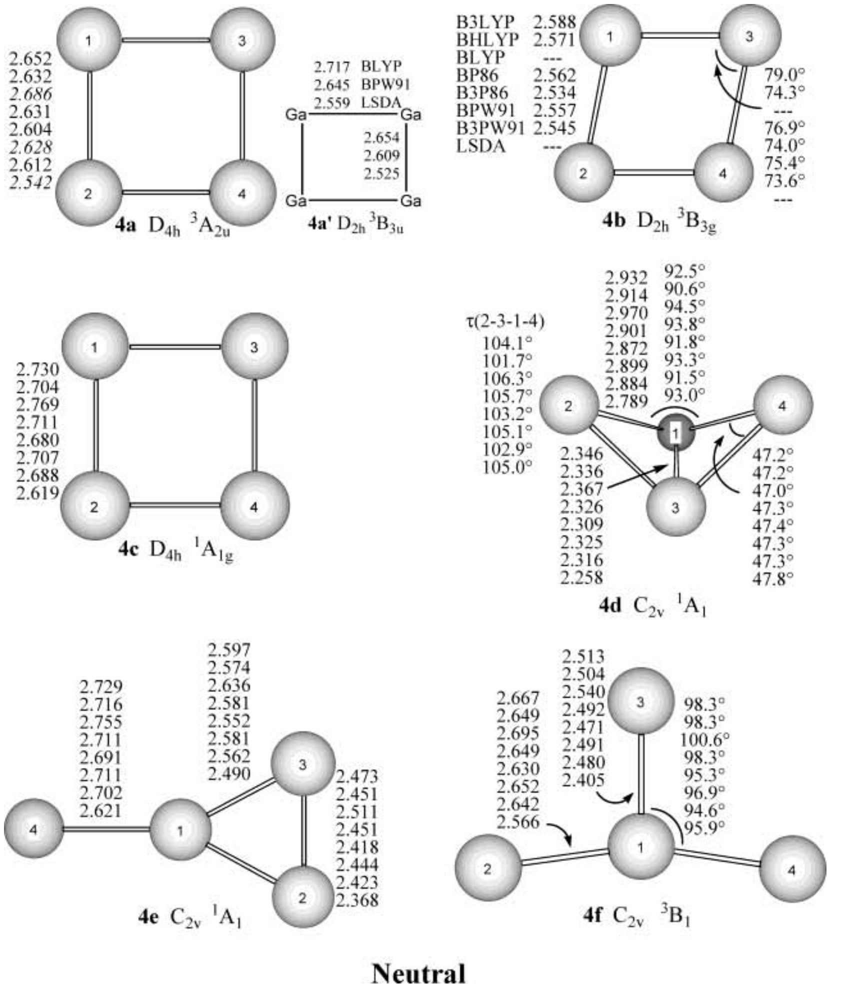


Figure 4. Molecular geometries for neutral Ga_4. All bond distances are in Å. Italic fonts for structure **4a** indicate that it is a transition state.

No experimental data are available for the Ga_3^- anion. Our theoretical results show that an equilateral triangular structure **3a**$^-$ (D_{3h} symmetry) in its closed-shell $^1A_1'$ ground state is the global minimum. The Ga−Ga bond distance (2.545 Å, BHLYP) for **3a**$^-$ is shorter than that of its neutral counterpart by ∼0.02 Å. This Ga_3^- anion bond distance is close to that predicted by Kuznetsov and Boldyrev[25] (2.550 Å by B3LYP/6-311+G* or 2.584 Å by CCSD(T)/6-311+G*). The triplet $^3B_2$ state forms an isosceles triangle structure (**3b**$^-$) lying at a higher energy than structure **3a**$^-$ by 3−8 kcal/mol. We also find that a linear structure (**3c**$^-$) with $^3\Sigma_g^-$ symmetry is a genuine minimum except in the LSDA method, which gives a pair of tiny degenerate imaginary vibrational frequencies (17i cm^{-1}). Structure **3c**$^-$ lies above the global minimum **3a**$^-$ in energy by ∼19 kcal/mol. Since structure **3a**$^-$ has two p electrons,[25] it might be considered an aromatic system and is rather stable.

The theoretical EA_{ad}, EA_{vert}, and VDE values are listed in Table 6. Our predicted VDE values for Ga_3 range from 1.94 to 2.28 eV with the DFT methods (similar to Ga_2/Ga_2^-, excluding BHLYP, B3P86, and LSDA). The BLYP, BPW91, and B3PW91 methods predict the values (1.94, 1.95, and 1.96 eV, respectively) closest to the experimental VDE of 1.95 ± 0.1 eV.[8] Kuznetsov and Boldyrev[25] predicted the VDE to be 1.69 eV at the CCSD(T)/6-311+G* level of theory. With a more nearly complete basis set, their CCSD(T) EA would certainly have been closer to the experimental values.

Ga_4 and Ga_4^-. For the tetramers, six geometries were considered and the optimized structures are reported in Figure 4. The relative energies of these structures are listed in Table 8. There are no experimental data available. Katircioğlu and Erkoç,[22] using a molecular-dynamics technique, suggested in 1989 that Ga_4 has a rhombus structure. Meier, Peyerimhoff, and Grein,[18] one year later, predicted the square and rhombus structures as being almost isoenergetic, with the square structure having the lower energy. The next year Balasubramanian and Feng[26] predicted the rhombus geometry ($^3B_{3u}$ state) to be the global minimum. Jones[24] also concluded that the global minimum is the rhombus (D_{2h}, triplet) structure, with the triplet square structure only 0.03 eV higher.

In the present work, the DFT methods predict that the global minimum is the square structure **4a** (D_{4h}, $^3A_{2u}$), with the exception that three functionals predict a tiny imaginary vibrational frequency: 40i (BLYP), 23i (BPW91), and 35i (LSDA). Following this normal mode, the latter three methods predict a rectangular structure (**4a′**) with D_{2h} symmetry in its $^3B_{3u}$ state. The other five methods predict the D_{4h} structure **4a** to have all real vibrational frequencies with the smallest being 6−70 cm^{-1}, indicating a genuine minimum on a very flat potential hypersurface. The Ga−Ga bond lengths of structure **4a** are 2.632 Å (BHLYP). The triplet rhombus structure (**4b**, D_{2h}, $^3B_{3g}$) is slightly higher in energy (2.9−4.4 kcal/mol) than the global minimum **4a** (or **4a′**). The four equal bond lengths of **4b** are 2.571 Å (BHLYP), and the acute bond angle is 74.3°. Katircioğlu and Erkoç[22] reported bond distances of 2.5 Å and acute bond angles of 61.6° with their molecular-dynamics method. Balasubramanian and Feng's[26] results are 2.65 Å and 88°, using the complete active-space multiconfiguration self-consistent field (CAS-MCSCF) followed by configuration

TABLE 8: Relative Energies (kcal/mol) for the Structures of the Ga_4 Cluster[a]

	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
4a	0.0	0.0	*0.0*	0.0	0.0	*0.0*	0.0	*0.0*
4b	4.4	5.4	*b*	2.9	3.6	3.0	3.6	*b*
4c	7.0	6.8	6.9	6.6	9.4	9.6	9.2	10.9
4d	10.6	9.6	10.7	12.5	12.4	12.6	12.2	12.2
4e	12.0	10.6	11.9	14.0	14.0	14.3	13.9	13.8
4f	13.8	10.6	13.9	16.9	16.4	16.7	15.7	*22.8*
4a$^-$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4b$^-$	0.1	-1.0	0.7	1.4	0.6	1.2	0.4	0.3
4c$^-$	*15.5*	*12.3* (12.2[c])	16.1	17.5	16.4	17.1	16.0	20.6
4d$^-$	16.8	14.7	16.6	18.9	*18.8*	*18.9*	18.4	*23.3*
4e$^-$	23.7	19.7	25.6	25.2	23.1	24.3	22.3	29.4

[a] Italics indicate the levels of theory at which **4a**, **4c$^-$**, **4d$^-$**, or **4f** is a transition state. [b] Not a stationary point. [c] The relative energy of **4c$^{-\prime}$**.

interaction calculations. Jones[24] predicted r_e(Ga−Ga) = 2.375 Å and an acute angle of 71.6°, using a combination of density functional (DF) calculations with finite-temperature molecular dynamics (MD). These results are in fair agreement with the present DFT computations. The singlet square structure **4c** (D_{4h}, $^1A_{1g}$) lies higher than the global minimum **4a** by 7−11 kcal/mol. Structure **4d** with C_{2v} symmetry in its $^1A_1$ state (reminiscent of bicyclobutane) is the only nonplanar structure. It lies higher in energy than the global minimum **4a** by 9.6−12.6 kcal/mol. Structures **4e** and **4f** are both planar structures, and have not been reported previously. Structure **4e** looks a bit like methylene cycloproane, while **4f** resembles the T-shaped BrF_3. Structures **4e** and **4f** are less stable than the global minimum **4a** by ∼14 and ∼17 kcal/mol, respectively. In summary, it seems that the change from closed structures to open structures raises the energy, and the lowest triplet state lies below the singlet for comparable structures.

For the Ga_4^- anion cluster, we report five structures, as shown in Figure 5. With the attachment of an electron to the neutral **4a** (D_{4h}, $^3A_{2u}$), the square anion **4b$^-$** (D_{4h}, $^2A_{2u}$; except for LSDA) is a minimum, and its sides are somewhat shorter than those for the neutral (by ∼0.05 Å). The $^2A_{1g}$ electronic state with D_{4h} symmetry is an excited electronic state, and it is a transition state. The $^2A_{1g}$ state collapses to a rectangular structure **4a$^-$** (D_{2h}, ^2A_g), which is another minimum nearly degenerate with **4b$^-$**. The square structure **4b$^-$** lies lower than **4a$^-$** by 1.0 kcal/mol with the BHLYP method, but structure **4a$^-$** is a global minimum with the other methods (see Table 8). Structure **4c$^-$** (C_2) in its ^2A state is a three-dimensional structure. It is predicted to be a minimum except in the B3LYP and BHLYP methods, which give one imaginary vibrational frequency. Following this imaginary mode, it leads to structure **4a$^-$** with B3LYP but to a new C_s structure (**4c$^{-\prime}$**) with the BHLYP method. Structure **4d$^-$** (C_{2v}) in its $^2B_2$ electronic state is a genuine minimum with the B3LYP, BHLYP, BLYP, BP86, and BPW91 methods, while there is a very small imaginary vibrational frequency with the other three methods: 4i (B3P86), 7i (B3PW91), and 22i (LSDA). Following this imaginary mode, **4d$^-$** leads to structure **4c$^-$**. Structure **4d$^-$** is less stable than the global minimum **4a$^-$** by 16−23 kcal/mol. The tetrahedral structure **4e$^-$** (T_d, $^4A_1$) is a local minimum, too, but it has a higher energy, lying above **4a$^-$** by 21−29 kcal/mol. There are no experimental or theoretical data available for Ga_4^- for comparison.

The theoretical EA_{ad} and EA_{vert} for **4a** (or **4a′** with BLYP, BPW91, and LSDA) and VDE for **4a$^-$** are reported in Table 6. The range of our predicted VDEs is from 1.83 to 2.23 eV. Like the Ga_2 cluster, the BP86 method predicted the VDE value (2.23 eV) closest to the experimental value (2.40 eV) by Cha et al.[8] The BP86 method predicts values of 2.14 eV for EA_{ad} and 2.06 eV for EA_{vert}. The small differences among the EA_{ad}, EA_{vert}, and VDE values are due to the similar geometries between neutral and anion species.

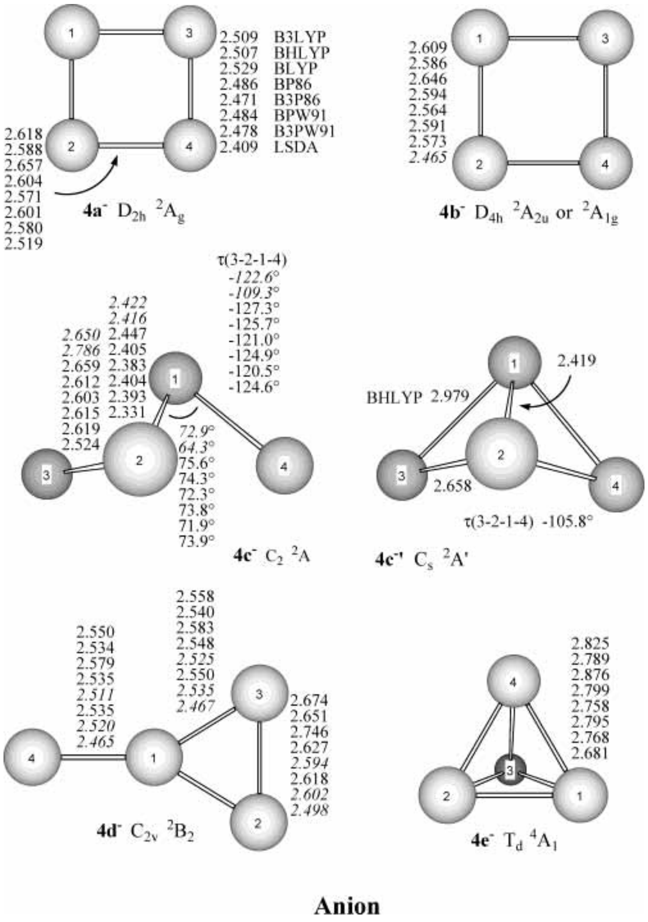


Figure 5. Molecular geometries for anionic Ga_4^-. All bond distances are in Å. Italic fonts for structure **4b$^-$**, **4c$^-$**, or **4d$^-$** indicate that it is a transition state.

Ga_5 and Ga_5^-. The favorable structures for the neutral Ga_5 and the anionic Ga_5^- are shown in Figures 6 and 7, respectively. We found four stationary points for neutral Ga_5. Structure **5a** with C_s symmetry for its $^2A'$ electronic state is the global minimum predicted by the B3LYP, BLYP, and BP86 methods, but it has one small imaginary vibrational frequency with the other five methods: 33i (BHLYP), 21i (B3P86), 9i (BPW91), 23i (B3PW91), and 21i (LSDA). Following the corresponding normal mode, **5a** collapses to structure **5a′** with the different methods. The B3P86, BPW91, and B3PW91 methods predict a C_1 structure **5a′** (Figure 5) only slightly distorted from structure **5a**, and the energy of **5a′** is lower than that of **5a** by <0.1 kcal/mol (Table 9). The BHLYP method predicts a peculiar C_s structure **5a′**, which has almost the same energy as **5a** (Table

TABLE 9: Relative Energies (kcal/mol) for the Structures of Ga$_5$[a]

	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
5a	0.0	*0.4*	0.0	0.0	*0.1*	*0.0*	*0.1*	*0.4*
5a′	same as **5a**	0.0	same as **5a**		0.0	0.0	0.0	0.0
5b	15.3	12.1	15.6	20.3	19.6	20.0	18.8	*30.1*
5b′	same as **5b**							26.8
5a$^-$	*0.0*	0.0	0.0	*0.2*	*0.1*	*0.2*	*0.1*	*0.5*
5b$^-$	0.0	same as **5a$^-$**		0.0	0.0	0.0	0.0	0.0
5c$^-$	20.9	19.9	*21.0*	*22.7*	22.6	*22.8*	22.4	*25.6*
5d$^-$	21.4	19.8	20.2	25.7	26.5	25.9	25.9	35.1

[a] Italics indicate the levels of theory at which the structures in question are transition states.

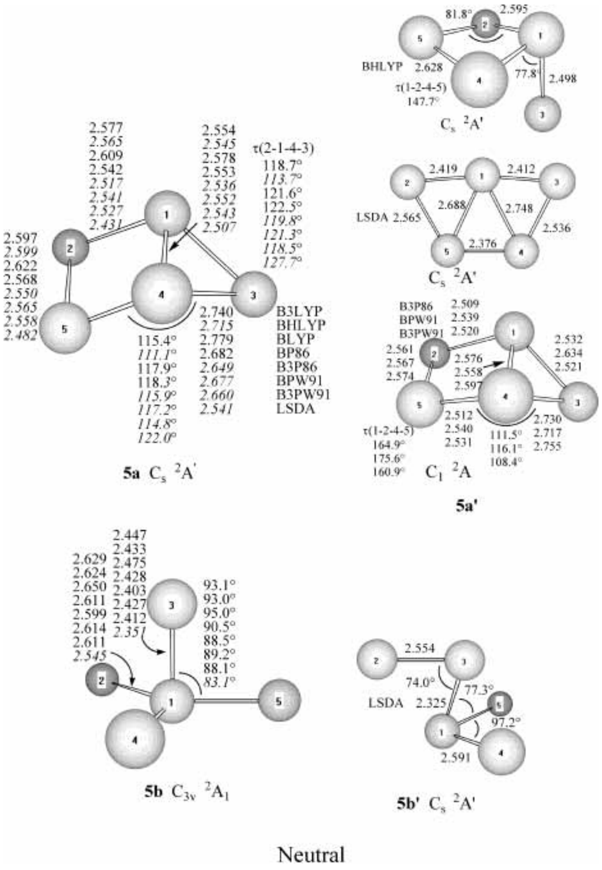


Figure 6. Molecular geometries for neutral Ga$_5$. All bond distances are in Å. Italic fonts for structures **5a** and **5b** indicate transition states.

9). The LSDA method predicts a planar structure (C_s, ^{2}A′) containing three triangles with an energy 0.6 kcal/mol lower than that of **5a**. (The LSDA energy of the constrained C_{2v} strucure lies higher than that of the C_s symmetry by ~0.14 kcal/mol.)

Structure **5b** with C_{3v} symmetry in its ^{2}A$_1$ state is a local minimum except in the LSDA method, which gives a pair of small degenerate imaginary vibrational frequencies (e mode, 18i cm^{-1}). Following this mode, LSDA predicts a C_s minimum **5b′**, which appears to be a less-reasonable structure. Throughout this work, we see similar problems with the LSDA method, which is so popular with physicists. Structure **5b** lies higher in energy than **5a** by 12−20 kcal/mol, while structure **5b′** (with LSDA) lies higher than structure **5a** by 27 kcal/mol. We also tried to optimize other possible structures as provided in the previous study of Jones,[24] such as a deformed pyramid (C_s and C_{4v}), the triangular biprism (D_{3h}), a planar structure (C_{2v}, like LSDA **5na′**), and so on, but none of these appears to be a stationary point. In 1993, Jones[24] reported the deformed pyramid (C_s) as the global minimum using the DFT method, but we predict that it collapses to structure **5a**. Our results are consistent with those reported by Gong and Tosatti[23] using their ab initio molecular-dynamics method. To our knowledge, there are no Ga$_5$ experimental data for comparison.

The global minimum for the Ga$_5^-$ anion is a planar structure **5a$^-$** (C_s, ^{1}A′) with the BHLYP and BLYP methods. However, in each of the other six DFT methods, there is one very small imaginary vibrational frequency [4i (B3LYP), 14i (BP86), 11i (B3P86), 14i (BPW91), 10i (B3PW91), and 21i (LSDA)], and it leads to a slightly distorted C_1 structure **5b$^-$**, with the terminal Ga atom somewhat out of the plane. Structure **5b$^-$** has nearly the same energy as **5a$^-$**, for example, within 0.5 kcal/mol. This structure is similar to a stable Ga$_5^-$ structure reported by Jones.[24] Both of the high-symmetry structures **5c$^-$** (a spiro structure of D_{2d} symmetry, ^{1}A$_1$ state) and **5d$^-$** (T_d symmetry, ^{1}A$_1$ state) have four Ga atoms connecting to a central Ga atom; however, **5c$^-$** has two small Ga−Ga−Ga angles (<60°), and it has one small degenerate imaginary vibrational frequency in each of the four DFT methods: 17i (BLYP), 19i (BP86), 20i (BPW91), and 8i (LSDA). Following this normal mode, we find our results lead to **5a$^-$** or **5b$^-$**. The highly symmetric tetrahedral structure **5d$^-$** is a minimum on its PES with all of the DFT methods, and it has almost the same energy as **5c$^-$** (lying lower than **5c$^-$** with the BHLYP and BLYP methods, but higher with the other DFT methods, Table 9). No experimental data are available.

The EA$_{\text{ad}}$, EA$_{\text{vert}}$, and VDE predictions are reported in Table 6. The present VDE is in the range from 2.03 to 2.32 eV. Cha et al.[8] have determined from photoelectron spectra the VDE of Ga$_5$ to be 2.45 ± 0.1 eV, and the BP86 method again makes the best prediction (2.32 eV). The BP86 EA$_{\text{ad}}$ value for the Ga$_5$ cluster is 2.27 eV, and the comparable EA$_{\text{vert}}$ is 2.23 eV. The EA$_{\text{ad}}$, EA$_{\text{vert}}$, and VDE values are very close to each other because the global minima for the neutral Ga$_5$ and anionic Ga$_5^-$ are notably similar in geometry.

Ga$_6$ and Ga$_6^-$. Five equilibrium geometries for neutral Ga$_6$ clusters and two for anionic Ga$_6^-$ are displayed in Figures 8 and 9, respectively. Their relative energies without ZPVE corrections (in kcal/mol) are listed in Table 10. No experimental geometries are available for either Ga$_6$ or Ga$_6^-$. Theoretically, Gong and Tosatti[23] applied an ab initio molecular-dynamics method and found the most stable structure to be a distorted prism **6a**. Jones[24] reported the ground state of Ga$_6$ was the trigonal antiprism (**6d**, D_{3d}) and predicted that the other structures are almost degenerate.

The present results show that the singlet structure **6a** (with C_{2v} symmetry) and the triplet structure **6b** (D_{3h}) have similar energies. Structure **6a** lies lower than **6b** with the B3LYP, BLYP, BP86, and LSDA methods, but higher than **6b** with the BHLYP, B3P86, BPW91, and B3PW91 methods (Table 10). The six triangle Ga−Ga bond distances in structure **6b** are longer than the distances [r(1−2) and r(3−4)] in structure **6a** by ~0.14 Å. Structures **6c** (C_s, ^{1}A′ state), **6d** (D_{3d}, ^{1}A$_{1g}$ state), and **6e** (D_{2d}, ^{1}A$_1$ state) are local minima. Of these, only **6e** has

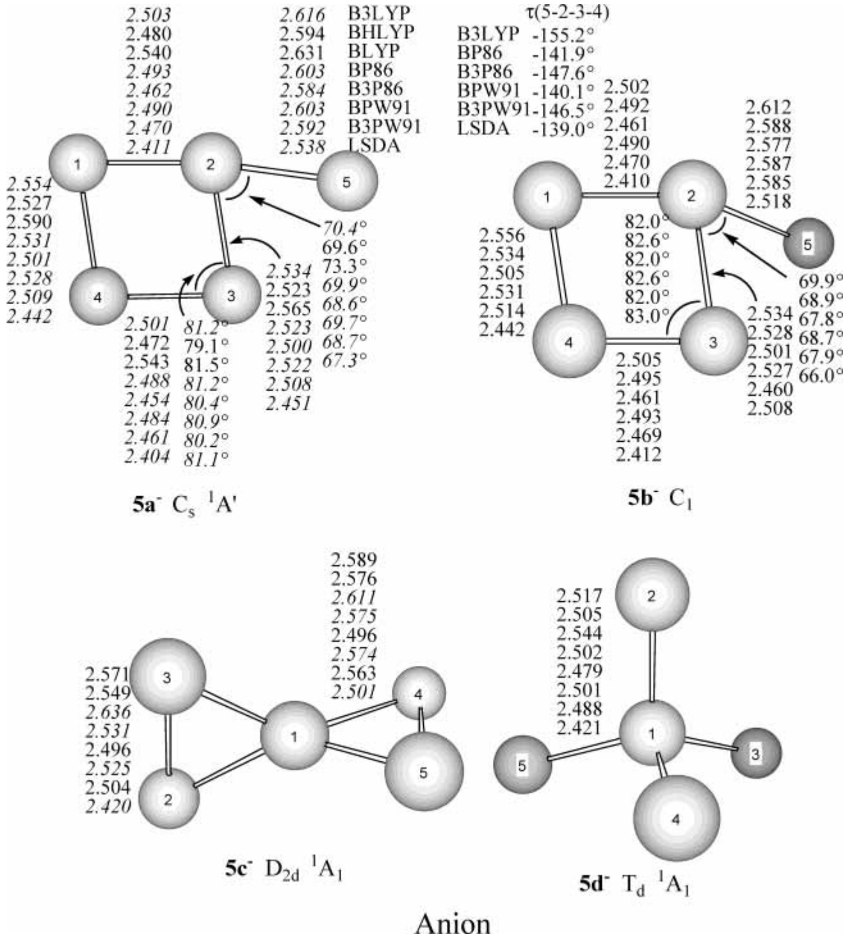


Figure 7. Molecular geometries for anionic Ga_5^-. All bond distances are in Å. Italic fonts for structures **5a**$^-$ and **5c**$^-$ indicate transition states.

TABLE 10: Relative Energies (kcal/mol) for the Different Structures of the Ga_6 Cluster

	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
6a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6b	0.6	−1.2	2.7	0.3	−1.3	−0.1	−1.4	0.8
6c	3.4	2.0	4.9	3.9	2.6	3.6	2.5	2.9
6d	4.5	3.9	6.0	3.2	2.2	2.5	1.8	0.6
6e	39.1	35.9	38.8	43.3	43.6	44.0	43.4	51.2
6a$^-$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6b$^-$	15.2	12.8	*a*	16.9	18.2	17.5	18.1	21.6

[a] Structure **6b**$^-$ collapses to **6a**$^-$ with the BLYP method.

a structure familiar to chemists, looking like a biscyclopropyl ethylene or something of the sort. Structure **6c** is more stable than **6d** with the B3LYP, BHLYP, and BLYP methods, while it is less stable than **6d** with the other five methods. Either way, the energy difference between the two is less than 2.5 kcal/mol, indicating that these two structures are close in energy (Table 10). The intriguing D_{2d} structure **6e** has not been reported before, but it has a much higher energy (about 40 kcal/mol) than **6a**. Structures **6a** and **6d** are qualitatively in agreement with the previously predicted distorted prism[23] and trigonal antiprism, respectively.[24] There were no bond distances reported by Gong and Tosatti,[23] and our bond lengths for **6d** are longer than those predicted by Jones. [24]

We located two structures of the anion Ga_6^- cluster. The apparent global minimum **6a**$^-$ (C_{2v} symmetry, $^2A_1$ state) has a geometry similar to that of the neutral global minimum. Structure **6b**$^-$ with C_i symmetry for the ^2A_g state is a local minimum, except with the BLYP method, which predicts a ^2A_u state with an imaginary vibrational frequency, leading eventually to **6a**$^-$. Structure **6b**$^-$ is less stable than structure **6a**$^-$ by about 13−22 kcal/mol (Table 10).

The theoretical EA_{ad}, EA_{vert}, and VDE values for the Ga_6/Ga_6^- clusters, as well as the experimental data, are listed in Table 6. The range of VDE is from 2.12 to 2.54 eV, and the B3PW91 value (2.54 eV) is closest to the experimental (2.60 ± 0.1 eV) value reported by Cha et al.[8] The BP86 EA_{ad} is 2.31 eV, and EA_{vert} is 2.02 eV. The values for EA_{ad}, EA_{vert}, and VDE are fairly similar due to the small differences in geometry between the neutral and anion species.

Dissociation Energies and Harmonic Vibrational Frequencies. The first bond dissociation energies for Ga_n/Ga_n^- ($n = 2-6$) are given in Tables 11 and 12. Table 11 shows the dissociation energies ($Ga_n \rightarrow Ga_{n-1} + Ga$) for the neutral species. As noted in the previous studies,[33,34] the theoretical dissociation energies predicted by the BHLYP method are usually too small, while those from the LSDA methods are too large, and both are unreliable. This is because the hybrid BHLYP functional incorporates the standard Hartree−Fock theory to the greatest degree of all the functionals used in this study, and it is well-known that the Hartree−Fock method performs poorly for bond-breaking processes.[56] To our surprise, therefore, for diatomic Ga_2, the BHLYP D_e(Ga−Ga) value (1.17 eV) is closest to the experimental values of 110.8 ± 4.9 kJ/mol (1.14 ± 0.05 eV)[9] and 110.3 ± 7 kJ/mol (1.14 ± 0.07 eV).[10] The most recently experimental upper limit $D_e \leq 8891\ \mathrm{cm^{-1}}$ (1.102 eV) obtained from electronic spectra by Tan and Dagdigian[5] appears definitive and is even lower. There are several theoretical D_e values for the Ga_2 dimer. In 1986, Balasubramanian[14] predicted the theoretical dissociation energy

TABLE 11: Dissociation Energies (D_e) for the Neutral Ga_n Species ($n = 2-6$) [eV (kcal/mol)][a]

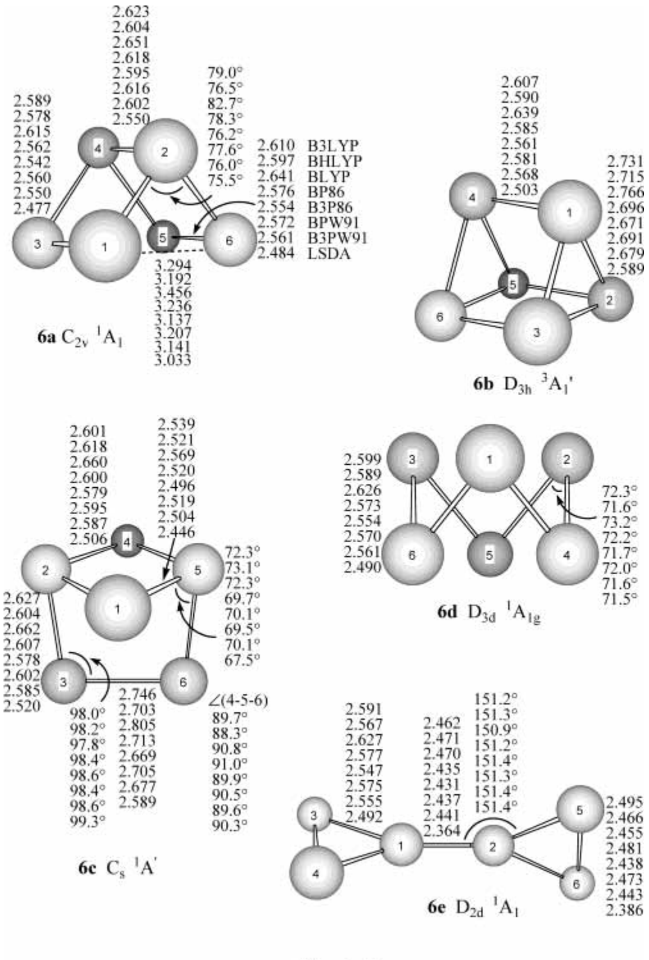
dissociation	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA	experiment
$Ga_2 \rightarrow Ga + Ga$	1.30 (30.1)	1.17 (27.0)	1.46 (33.6)	1.53 (35.4)	1.47 (33.8)	1.48 (34.1)	1.40 (32.3)	1.95 (45.1)	<1.102[b] <1.5[c] 1.14[d]
$Ga_3 \rightarrow Ga_2 + Ga$	1.58 (36.4)	1.37 (31.5)	1.68 (38.7)	1.92 (44.2)	1.84 (42.4)	1.83 (42.1)	1.73 (39.9)	2.80 (64.6)	
$Ga_4 \rightarrow Ga_3 + Ga$	1.98 (45.7)	1.78 (41.1)	2.10 (48.3)	2.27 (52.4)	2.20 (50.8)	2.22 (51.3)	2.13 (49.1)	2.77 (63.9)	
$Ga_5 \rightarrow Ga_4 + Ga$	1.80 (41.5)	1.63 (37.6)	1.90 (43.9)	2.14 (49.4)	2.08 (47.9)	2.08 (48.0)	1.99 (45.9)	3.02 (69.6)	
$Ga_6 \rightarrow Ga_5 + Ga$	2.29 (52.7)	2.06 (47.5)	2.38 (54.8)	2.67 (61.7)	2.62 (60.5)	2.63 (60.7)	2.54 (58.6)	3.51 (80.9)	

[a] Values are not corrected with ZPVE. [b] From ref 5. [c] From ref 11−13. [d] From refs 9 and 10.

TABLE 12: Dissociation Energies (D_e) for the Anionic Ga_n^- Species ($n = 2-6$) [eV (kcal/mol)][a]

dissociation	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
$Ga_2^- \rightarrow Ga + Ga^-$	2.18 (50.2)	2.07 (47.8)	2.23 (51.4)	2.45 (56.6)	2.45 (56.6)	2.40 (55.3)	2.35 (54.3)	2.99 (69.1)
$Ga_3^- \rightarrow Ga_2 + Ga^-$	2.85 (65.7)	2.68 (61.8)	2.84 (65.6)	3.12 (71.9)	3.11 (71.8)	2.98 (68.8)	2.94 (67.9)	4.13 (95.2)
$Ga_4^- \rightarrow Ga_3 + Ga^-$	3.52 (81.1)	3.32 (76.5)	3.53 (81.5)	3.82 (88.2)	3.82 (88.0)	3.74 (86.3)	3.67 (84.7)	4.60 (106.0)
$Ga_5^- \rightarrow Ga_4 + Ga^-$	3.50 (80.8)	3.38 (78.0)	3.48 (80.2)	3.83 (88.2)	3.86 (88.9)	3.74 (86.3)	3.71 (85.5)	4.84 (111.7)
$Ga_6^- \rightarrow Ga_5 + Ga^-$	4.00 (92.1)	3.91 (90.3)	3.86 (89.1)	4.39 (101.3)	4.52 (104.1)	4.35 (100.3)	4.38 (100.9)	5.42 (125.0)
$Ga_3^- \rightarrow Ga_2^- + Ga$	1.97 (45.5)	1.78 (41.1)	2.07 (47.8)	2.20 (50.7)	2.13 (49.1)	2.06 (47.6)	1.99 (46.0)	3.09 (71.2)
$Ga_4^- \rightarrow Ga_3^- + Ga$	2.25 (51.8)	2.00 (46.2)	2.37 (54.7)	2.63 (60.5)	2.54 (58.6)	2.58 (59.6)	2.46 (56.7)	3.27 (75.3)
$Ga_5^- \rightarrow Ga_4^- + Ga$	1.97 (45.4)	1.85 (42.6)	2.04 (47.0)	2.27 (52.4)	2.24 (51.7)	2.22 (51.3)	2.16 (49.8)	3.02 (69.6)
$Ga_6^- \rightarrow Ga_5^- + Ga$	2.29 (52.9)	2.16 (49.9)	2.29 (52.7)	2.71 (62.5)	2.74 (62.5)	2.69 (62.0)	2.66 (62.0)	3.60 (82.9)

[a] Values are not corrected with ZPVE.


6a C_{2v} $^1A_1$

6b D_{3h} $^3A_1'$

6c C_s $^1A'$

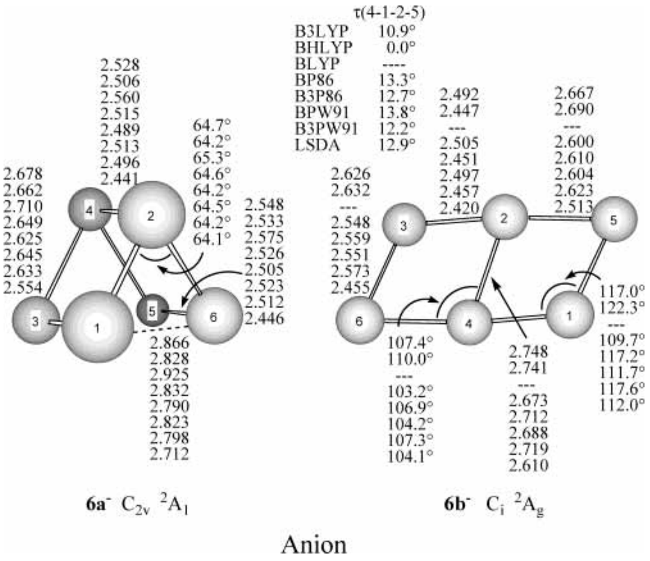
6d D_{3d} $^1A_{1g}$

6e D_{2d} $^1A_1$

Neutral

Figure 8. Molecular geometries for neutral Ga_6. All bond distances are in Å.

of Ga_2 to be 1.18 eV using the CASSCF method followed by the first-order configuration interaction (FOCI). Later, in 1990, Balasubramanian[15] predicted $D(Ga_2)$ to be 1.2 eV using CASSCF followed by the second-order configuration interaction (SOCI). A more recent value is 1.17 eV given by Das[19] from MRD-CI methods in 1997. In 1998, Ghosh, Tanaka, and


6a⁻ C_{2v} $^2A_1$

6b⁻ C_i ^2A_g

Anion

Figure 9. Molecular geometries for anionic Ga_6^-. All bond distances are in Å.

Mochizuki[20] reported a value of 1.28 eV using MRSDCI and MRCPA methods with an extensive basis set. The above theoretical results appear slightly lower than our DFT results. Our B3LYP result (1.30 eV) is in good agreement with the MRSDCI value.[20]

For the neutral clusters, our B3LYP theoretical first dissociation energies are predicted to be 1.58 eV for Ga_3, 1.98 eV for Ga_4, 1.80 eV for Ga_5, and 2.29 eV for Ga_6. To our knowledge, there are no experimental results for these species. Theoretically, Balasubramanian and Feng[26] reported the dissociation energy for $Ga_4 \rightarrow Ga_3 + Ga$ as 1.4 eV with the CAS-MCSCF method.

For the anions, Ga_n^-, there are two distinct types of dissociation, for example, the dissociation to a neutral Ga_{n-1} and the atomic anion Ga^- and the dissociation to the ionic cluster Ga_{n-1}^- and a neutral Ga atom. Except for LSDA, the other seven methods predict values broadly consistent with each other. The B3LYP $D_e(Ga_2^-)$ value is 2.18 eV, consistent with the previous theoretical value (2 eV) reported by Balasubramanian[15] at the MCSCF/FOCI (SOCI) levels. For the other Ga_n^- anions, to our knowledge, there are no experimental and theoretical dissocia-

TABLE 13: Predicted Harmonic Vibrational Frequencies (cm^{-1}) for the Global Minima of the Neutral and Anionic Ga$_n$ (n = 3−6) Clusters

	sym	B3LYP	BHLYP	BLYP	BP86	B3P86	BPW91	B3PW91	LSDA
3a	a_1	55	67	44	55	69	58	69	72
	b_2	168	166	159	174	181	175	178	196
	a_1	171	180	162	177	189	179	187	204
3a$^-$	e'	122	131	111	123	131	122	129	140
	a_1'	203	210	191	212	221	213	218	240
4a	b_{2g}	58	59	40i	6	70	23i	59	35i
	b_{1g}	52	43	64	56	47	53	44	51
	b_{2u}	63	91	64	62	60	61	64	59
	e_u	147	146	142	153	158	154	156	176
	a_{1g}	165	174	155	169	178	170	177	192
4a$^-$	b_{3g}	55	32	63	53	39	49	36	43
	a_u	78	80	75	77	80	77	78	82
	b_{2u}	157	152	141	155	166	157	164	176
	a_g	172	161	165	179	179	180	180	197
	b_{1u}	181	181	174	189	194	191	192	209
	a_g	188	193	188	199	200	200	198	216
5a	a''	16	33i	21	4	21i	9i	23i	21i
	a'	25	26	24	25	26	26	26	25
	a''	68	67	68	67	67	66	66	70
	a'	94	94	90	96	101	95	98	118
	a''	97	102	93	100	109	101	108	127
	a'	157	154	150	166	171	168	169	191
	a''	163	163	155	175	182	176	179	202
	a'	177	182	167	180	189	182	187	208
	a'	188	196	177	195	206	197	204	228
5a$^-$	e	13	22	17i	19i	15	20i	13	8i
	b_1	39	39	38	40	41	41	41	45
	a_1	74	79	59	82	89	84	89	100
	e	125	146	102	114	136	116	135	131
	b_2	135	147	111	146	160	149	159	177
	a_1	161	170	144	171	182	173	180	200
	b_2	247	260	231	251	264	253	262	279
6a	b_2	41	38	43	42	42	43	41	42
	a_2	42	36	45	43	39	41	38	41
	a_1	56	66	45	60	70	63	71	77
	a_2	84	87	79	86	89	86	88	95
	b_2	85	85	85	84	86	84	85	90
	a_1	136	137	130	139	144	141	143	154
	b_1	147	149	139	157	163	159	161	180
	a_2	151	154	147	157	162	157	160	172
	b_2	170	174	160	179	187	182	186	204
	a_1	173	181	162	180	189	182	187	204
	b_1	181	189	172	187	196	189	195	207
	a_1	185	195	171	193	203	195	202	219
6a$^-$	a_2	28	21	33	26	21	23	18	24
	b_2	66	65	62	72	74	73	73	82
	a_2	94	94	92	95	97	95	96	102
	b_2	96	98	94	96	99	95	98	104
	a_1	98	105	89	102	109	104	109	116
	b_1	106	77	116	125	114	126	113	151
	a_2	109	111	104	113	118	114	117	131
	b_2	156	161	148	164	172	166	170	191
	a_1	166	171	156	171	179	173	177	191
	b_1	168	173	159	175	182	177	181	194
	a_1	173	180	163	179	188	181	186	205
	a_1	196	206	183	200	211	202	209	221

tion energies available. Our results should provide a benchmark for future experimental studies.

Harmonic vibrational frequencies have been predicted for each neutral and anionic molecule with the eight functionals. The vibrational frequencies for the Ga_2/Ga_2^- systems are reported in Table 3. Available experimental[7] and previous theoretical vibrational frequencies[10,14,15,18−20,24] are also included in Table 3 for comparison. The BHLYP method gives the largest Ga_2 frequency (167 cm^{-1}) for **2a**, and it is the closest to experiment (180 cm^{-1}). The fact that the HF/DFT hybrid functionals produce higher vibrational frequencies than the pure exchange functional methods has been observed in many studies.[32−34] For other Ga_n/Ga_n^- (n = 3−6) systems, the vibrational frequencies for the global minima are reported in Table 13, and those for other structures are reported in Supporting Information. There are no experimental data available for comparison. Again, these vibrational predictions should be very helpful as guides for future experimental studies. In light of the increasing importance of gallium in microelectronics technology, such experimental studies are seriously needed. These, in turn, will yield a more complete understanding of the reliability of the eight DFT methods for small metal clusters.

Conclusions

The present work provides a systematic study of the gallium clusters Ga_n ($n = 2-6$), consisting of 37 structures, each examined with eight different DFT methods. We found that for those Ga_n clusters with $n = 1-4$, high-spin electronic states are more favorable than low-spin states. The global minima for Ga_3 and Ga_4 are triangular and planar rectangular structures, respectively, while the global minima for Ga_5 and Ga_6 are nonplanar structures with low-spin electronic states. The BHLYP method predicts bond distances closest to experiment. In the prediction of bond lengths, the eight DFT methods consistently follow the order BLYP > B3LYP > BHLYP > BP86 > BPW91 > B3PW91 > B3P86 > LSDA. The BHLYP method predicts the closest bond distances to the most reliable previous theoretical studies. The BP86 method predicts VDE values [1.63 (Ga_2), 1.79 (Ga_3), 2.23 (Ga_4), 2.32 (Ga_5), and 2.53 eV (Ga_6)] that are closest in agreement with experimental values, and it must be considered the most reliable method for predicting the electron affinities of gallium clusters.

The B3LYP first dissociation energies for the neutral gallium clusters $D(Ga_{n-1} - Ga)$, excluding LSDA values, are 1.30 (Ga_2), 1.58 (Ga_3), 1.98 (Ga_4), 1.80 (Ga_5), and 2.29 eV (Ga_6). The dissociation energies necessary for the anionic Ga_n^- systems to lose a Ga atom are 2.18 (Ga_2^-), 1.97 (Ga_3^-), 2.25 (Ga_4^-), 1.97 (Ga_5^-), and 2.29 eV (Ga_6^-). The dissociation energies required for the loss of a Ga^- anion are larger: 2.85 (Ga_3^-), 3.52 (Ga_4^-), 3.50 (Ga_5^-), and 4.00 eV (Ga_6^-). Dissociation to $Ga_{n-1}^- +$ Ga is much easier, since the Ga_{n-1} cluster has a much larger EA than the Ga atom.

Since there are few experimental results available for the Ga_n/Ga_n^- systems, the present systematic theoretical predictions should provide strong motivation for further experimental studies for these important gallium clusters and their anions.

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Supporting Information Available: Tables for the predicted harmonic vibrational frequencies for the neutral and anionic Ga_3-Ga_6 clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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