

Predictions of ground states of LiGa and NaGa

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Abstract

The ground and very low-lying excited states of LiGa and NaGa have been studied using high level ab initio techniques. At the QCISD(T)/6-311 + G(2df) level of theory, the $^1\Sigma^+$ state was found to be the most stable for both molecules. The equilibrium bond lengths and dissociation energies were found to be: $R(\text{Li-Ga}) = 2.865 \text{ \AA}$ and $D_0(\text{LiGa}) = 22.3 \text{ kcal/mol}$ and $R(\text{Na-Ga}) = 3.174 \text{ \AA}$ and $D_0(\text{NaGa}) = 17.1 \text{ kcal/mol}$. Trends within the ground electronic states of LiB, NaB, LiAl, NaAl, LiGa and NaGa are discussed and predictions for related AlkM (Alk = Li–Cs and M = B–Tl) species are made.

1. Introduction

Recently we created, from published experimental and high level theoretical data, a Diatomic Periodic Table covering all main group elements [1]. Surprisingly, the ground electronic states and corresponding bond lengths (R_e) and dissociation energies (D_e) had not been established for many of these molecules. In a previous paper [2], we theoretically predicted the ground electronic states for ten diatomic molecules to complete the knowledge base of ground electronic states of diatomic molecules composed of first and second row atoms. However, beyond the second row, the number of diatomics with unknown ground states remains very large.

In some cases, the ground electronic state can be predicted reliably based on the Aufbau principle. However as we have already mentioned [2], a large number of anti-Aufbau ground electronic states occur in diatomics composed of electropositive atoms [3,4]. A remarkable example is provided by the series LiB, NaB, LiAl and NaAl. The ab initio studies on LiB by Kaufman and Sach [5] assumed a

$^1\Sigma^+$ ground state. However, the energy of LiB was found to be above that of the separated atoms. Cade and Huo [6], using a large Slater basis set, also calculated only the $^1\Sigma^+$ state for LiB and found an energy at the minimum slightly lower than that of the separated atoms. Nemukhin et al. [7] studied four electronic states in LiB: $^1\Sigma^+$, $^3\Pi_r$, $^3\Sigma^+$ and $^1\Pi_r$ at the CASSCF level with double zeta basis sets and found the $^3\Pi_r$ high-spin state to be the most stable with the $^1\Sigma^+$ low-spin state as the first excited state. In other subsequent high quality calculations [8–10], this theoretical prediction was confirmed.

NaB was found also to have a $^3\Pi_r$ high spin ground state [2]. However the isoelectronic LiAl and NaAl molecules have been theoretically predicted to have $^1\Sigma^+$ low-spin ground states, which has been experimentally verified [11,12]. At this time, the high-spin states for LiB and NaB remain theoretical predictions that have yet to be experimentally verified.

Taking into account these complicated results for these valence isoelectronic molecules, it remains difficult to predict the ground electronic state for AB

molecules, in which A is an alkali metal atom Li, Na, K, Rb, or Cs and B is Ga, In or Tl, because, while the electron affinities (EA) and ionization potentials (IP) change regularly in the Li–Na–K–Rb–Cs series, they vary irregularly in the B–Al–Ga–In–Tl series [13,14]. We therefore undertook the task of using high level ab initio methods to predict here that LiGa and NaGa (and probably KGa, RbGa and CsGa) have low-spin singlet ground electronic states.

2. Computational details

The bond lengths and harmonic vibrational frequencies were optimized using analytical gradients [15] and polarized split-valence basis sets of 6-311 + G* and 6-311 + G(2df) [16–19] quality at the correlated MP2(full) (UMP2(full) for open-shell systems),

QCISD and QCISD(T) [20] levels of theory. The UHF wave functions for open-shell systems were spin-projected to produce pure spectroscopic states (PUHF, PMP2, PMP3 and PMP4) [21,22]. All calculations were carried out with the GAUSSIAN 94 [23] suite of programs and the core orbitals were kept frozen in all correlated calculations unless otherwise specified.

3. Ground and lowest excited states of LiGa and NaGa

We studied LiGa and NaGa assuming double occupancy for the 1σ valence orbital, the two other valence electrons being distributed throughout the 2σ , 3σ and 1π valence orbitals giving four possible occupancies: $1\sigma^2 2\sigma^2$, $1\sigma^2 2\sigma^1 1\pi^1$, $1\sigma^2 2\sigma^1 3\sigma^1$,

Table 1
Calculated molecular properties of the lowest LiGa and LiGa⁺ states

LiGa ($^1\Sigma^+$)	LiGa ($^3\Pi_r$)	LiGa ($^3\Sigma^-$)	LiGa ⁺ ($^2\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^0 3\sigma^0$	$1\sigma^2 2\sigma^1 1\pi^1 3\sigma^0$	$1\sigma^2 2\sigma^0 1\pi^2 3\sigma^0$	$1\sigma^2 2\sigma^1 1\pi^0 3\sigma^0$
MP2(full)/6-311 + G*	MP2(full)/6-311 + G*	MP2(full)/6-311 + G*	MP2(full)/6-311 + G*
$E_{\text{MP2}} = -1931.092401$	$E_{\text{MP2}} = -1931.090818$	$E_{\text{MP2}} = -1931.063954$	$E_{\text{MP2}} = -1930.913023$
$R_e(\text{Li-Ga}) = 2.848 \text{ \AA}$	$R_e(\text{Li-Ga}) = 2.594 \text{ \AA}$	$R_e(\text{Li-Ga}) = 2.322 \text{ \AA}$	$R_e(\text{Li-Ga}) = 3.019 \text{ \AA}$
$\omega_e = 297 \text{ cm}^{-1}$	$\omega_e = 320 \text{ cm}^{-1}$	$\omega_e = 418 \text{ cm}^{-1}$	$\omega_e = 214 \text{ cm}^{-1}$
	$\langle S^2 \rangle = 2.018$	$\langle S^2 \rangle = 2.016$	$\langle S^2 \rangle = 0.770$
$T_{\text{eMP2(full)}} = 0.0 \text{ eV}$	$T_{\text{eMP2(full)}} = 0.04 \text{ eV}$	$T_{\text{eMP2(full)}} = 0.77 \text{ eV}$	$\text{IP}_{\text{aMP2(full)}} = 4.88 \text{ eV}$
QCISD/6-311 + G*	QCISD/6-311 + G*	QCISD/6-311 + G*	QCISD/6-311 + G*
$E_{\text{QCISD}} = -1930.689271$	$E_{\text{QCISD}} = -1930.680980$	$E_{\text{QCISD}} = -1930.653648$	$E_{\text{QCISD}} = -1930.504159$
$R_e(\text{Li-Ga}) = 2.874 \text{ \AA}$	$R_e(\text{Li-Ga}) = 2.637 \text{ \AA}$	$R_e(\text{Li-Ga}) = 2.353 \text{ \AA}$	$R_e(\text{Li-Ga}) = 3.058 \text{ \AA}$
$\omega_e = 283 \text{ cm}^{-1}$	$\omega_e = 305 \text{ cm}^{-1}$	$\omega_e = 408 \text{ cm}^{-1}$	$\omega_e = 212 \text{ cm}^{-1}$
	$\langle S^2 \rangle = 2.019$	$\langle S^2 \rangle = 2.016$	$\langle S^2 \rangle = 0.770$
$T_{\text{eQCISD}} = 0.0 \text{ eV}$	$T_{\text{eQCISD}} = 0.23 \text{ eV}$	$T_{\text{eQCISD}} = 0.96 \text{ eV}$	$\text{IP}_{\text{aQCISD}} = 5.04 \text{ eV}$
QCISD(T)/6-311 + G(2df)	QCISD(T)/6-311 + G(2df)	QCISD(T)/6-311 + G(2df)	QCISD(T)/6-311 + G(2df)
//QCISD(T)/6-311 + G(2df)	//QCISD(T)/6-311 + G(2df)	//QCISD(T)/6-311 + G(2df)	//QCISD(T)/6-311 + G*
$R_e(\text{Li-Ga}) = 2.865 \text{ \AA}$	$R_e(\text{Li-Ga}) = 2.624 \text{ \AA}$	$R_e(\text{Li-Ga}) = 2.353 \text{ \AA}$	$R_e(\text{Li-Ga}) = 3.058 \text{ \AA}$
$E_{\text{PMP2}} = -1930.671636$	$E_{\text{PMP2}} = -1930.670004$	$E_{\text{PMP2}} = -1930.642719$	$E_{\text{PMP2}} = -1930.492704$
$E_{\text{PMP3}} = -1930.685429$	$E_{\text{PMP3}} = -1930.680509$	$E_{\text{PMP3}} = -1930.653781$	$E_{\text{PMP3}} = -1930.500606$
$E_{\text{PMP4}} = -1930.690695$	$E_{\text{PMP4}} = -1930.684389$	$E_{\text{PMP4}} = -1930.657842$	$E_{\text{PMP4}} = -1930.503769$
$E_{\text{QCISD}} = -1930.691426$	$E_{\text{QCISD}} = -1930.683173$	$E_{\text{QCISD}} = -1930.656489$	$E_{\text{QCISD}} = -1930.503976$
$E_{\text{QCISD(T)}} = -1930.694002$	$E_{\text{QCISD(T)}} = -1930.685439$	$E_{\text{QCISD(T)}} = -1930.659049$	$E_{\text{QCISD(T)}} = -1930.504746$
	$\langle S^2 \rangle = 2.019$	$\langle S^2 \rangle = 2.019$	$\langle S^2 \rangle = 0.771$
$T_{\text{ePMP2}} = 0.0 \text{ eV}$	$T_{\text{ePMP2}} = 0.04 \text{ eV}$	$T_{\text{ePMP2}} = 0.79 \text{ eV}$	$\text{IP}_{\text{aPMP2}} = 4.87 \text{ eV}$
$T_{\text{ePMP3}} = 0.0 \text{ eV}$	$T_{\text{ePMP3}} = 0.13 \text{ eV}$	$T_{\text{ePMP3}} = 0.86 \text{ eV}$	$\text{IP}_{\text{aPMP3}} = 5.03 \text{ eV}$
$T_{\text{ePMP4}} = 0.0 \text{ eV}$	$T_{\text{ePMP4}} = 0.17 \text{ eV}$	$T_{\text{ePMP4}} = 0.89 \text{ eV}$	$\text{IP}_{\text{aPMP4}} = 5.09 \text{ eV}$
$T_{\text{eQCISD}} = 0.0 \text{ eV}$	$T_{\text{eQCISD}} = 0.22 \text{ eV}$	$T_{\text{eQCISD}} = 0.95 \text{ eV}$	$\text{IP}_{\text{aQCISD}} = 5.10 \text{ eV}$
$T_{\text{eQCISD(T)}} = 0.0 \text{ eV}$	$T_{\text{eQCISD(T)}} = 0.23 \text{ eV}$	$T_{\text{eQCISD(T)}} = 0.95 \text{ eV}$	$\text{IP}_{\text{aQCISD(T)}} = 5.15 \text{ eV}$

and $1\sigma^2 1\pi^2$, which lead to several low-lying electronic states: ${}^3\Pi_r$ ($1\sigma^2 2\sigma^1 1\pi^1$), ${}^1\Sigma^+$ ($1\sigma^2 2\sigma^2$), ${}^3\Sigma^+$ ($1\sigma^2 2\sigma^1 3\sigma^1$), and ${}^3\Sigma^-$ ($1\sigma^2 1\pi^2$). The first three states have the same Li(2S) + Ga (2P) asymptote, and the ${}^3\Sigma^-$ state has the Li(2P) + Ga (2P) asymptote. We did not consider the ${}^1\Pi_r$ ($1\sigma^2 2\sigma^1 1\pi^1$) state because we expect it to be higher in energy than ${}^3\Pi_r$ ($1\sigma^2 2\sigma^1 1\pi^1$) and therefore not important for determination of the ground state. Moreover, in extensive MRCI calculations on LiB, Ricca and Bauschlicher [10] have shown that the singlet ${}^1\Pi_r$ state is substantially higher in energy than the ${}^3\Pi_r$.

Results of our calculations for the ${}^1\Sigma^+$, ${}^3\Pi_r$, and ${}^3\Sigma^-$ states of LiGa and NaGa are presented in Tables 1 and 2, respectively. The ${}^1\Sigma^+$ state was found to be the ground state for both molecules. The

lowest excited ${}^3\Pi_r$ state lies at 5.4 kcal/mol (0.23 eV) for LiGa and at 5.5 kcal/mol (0.24 eV) for NaGa. The ${}^3\Sigma^+$ state was found to be repulsive for both species while the ${}^3\Sigma^-$ states were found to have minima 21.9 kcal/mol (0.95 eV) for LiGa and 23.6 kcal/mol (1.02 eV) for NaGa less stable than the ground state.

Therefore, for LiGa and NaGa, we found ${}^1\Sigma^+$ low-spin ground states. Our calculated rotational constants $B_e = 9.6718$ GHz (LiGa) and $B_e = 2.9096$ GHz (NaGa) and harmonic vibrational frequencies $\omega_e = 283$ cm^{-1} (LiGa) and $\omega_e = 152$ cm^{-1} (NaGa) may help in the identification of these molecules in gas phase or matrix isolation experiments. The calculated dissociation energies were found to be $D_0(\text{LiGa}) = 22.3$ kcal/mol and $D_0(\text{NaGa}) = 17.1$ kcal/mol (at the QCISD(T)/6-311 + G(2df) level

Table 2
Calculated molecular properties of the lowest NaGa and NaGa⁺ states

NaGa (${}^1\Sigma^+$)	NaGa (${}^3\Pi_r$)	NaGa (${}^3\Sigma^-$)	NaGa ⁺ (${}^2\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^0 3\sigma^0$	$1\sigma^2 2\sigma^1 1\pi^1 3\sigma^0$	$1\sigma^2 2\sigma^0 1\pi^2 3\sigma^0$	$1\sigma^2 2\sigma^1 1\pi^0 3\sigma^0$
MP2(full)/6-311 + G*	MP2(full)/6-311 + G*	MP2(full)/6-311 + G*	MP2(full)/6-311 + G*
$E_{\text{MP2}} = -2085.617162$	$E_{\text{MP2}} = -2085.614642$	$E_{\text{MP2}} = -2085.584093$	$E_{\text{MP2}} = -2085.446910$
$R_e(\text{Na-Ga}) = 3.113$ Å	$R_e(\text{Na-Ga}) = 2.957$ Å	$R_e(\text{Na-Ga}) = 2.660$ Å	$R_e(\text{Na-Ga}) = 3.358$ Å
$\omega_e = 166$ cm^{-1}	$\omega_e = 157$ cm^{-1}	$\omega_e = 218$ cm^{-1}	$\omega_e = 118$ cm^{-1}
	$\langle S^2 \rangle = 2.021$	$\langle S^2 \rangle = 2.012$	$\langle S^2 \rangle = 0.767$
$T_{\text{eMP2(full)}} = 0.0$ eV	$T_{\text{eMP2(full)}} = 0.07$ eV	$T_{\text{eMP2(full)}} = 0.90$ eV	$I_{\text{aMP2(full)}} = 4.63$ eV
QCISD/6-311 + G*	QCISD/6-311 + G*	QCISD/6-311 + G*	QCISD/6-311 + G*
$E_{\text{QCISD}} = -2085.094656$	$E_{\text{QCISD}} = -2085.086550$	$E_{\text{QCISD}} = -2085.056124$	$E_{\text{QCISD}} = -2084.92013$
$R_e(\text{Na-Ga}) = 3.176$ Å	$R_e(\text{Na-Ga}) = 3.021$ Å	$R_e(\text{Na-Ga}) = 2.699$ Å	$R_e(\text{Na-Ga}) = 3.408$ Å
$\omega_e = 152$ cm^{-1}	$\omega_e = 145$ cm^{-1}	$\omega_e = 211$ cm^{-1}	$\omega_e = 117$ cm^{-1}
	$\langle S^2 \rangle = 2.021$	$\langle S^2 \rangle = 2.012$	$\langle S^2 \rangle = 0.767$
$T_{\text{eQCISD}} = 0.0$ eV	$T_{\text{eQCISD}} = 0.22$ eV	$T_{\text{eQCISD}} = 1.05$ eV	$I_{\text{aQCISD}} = 4.75$ eV
QCISD(TQ)/6-311 + G(2df) //QCISD(T)/6-311 + G(2df)	QCISD(TQ)/6-311 + G(2df) //QCISD(T)/6-311 + G(2df)	QCISD(TQ)/6-311 + G(2df) //QCISD(T)/6-311 + G(2df)	QCISD(TQ)/6-311 + G(2df) //QCISD(T)/6-311 + G*
$R_e(\text{Na-Ga}) = 3.174$ Å	$R_e(\text{Na-Ga}) = 2.997$ Å	$R_e(\text{Na-Ga}) = 2.699$ Å	$R_e(\text{Na-Ga}) = 3.408$ Å
$E_{\text{PMP2}} = -2085.077392$	$E_{\text{PMP2}} = -2085.075221$	$E_{\text{PMP2}} = -2085.045875$	$E_{\text{PMP2}} = -2084.908458$
$E_{\text{PMP3}} = -2085.090978$	$E_{\text{PMP3}} = -2085.085589$	$E_{\text{PMP3}} = -2085.056716$	$E_{\text{PMP3}} = -2084.916495$
$E_{\text{PMP4}} = -2085.096237$	$E_{\text{PMP4}} = -2085.089449$	$E_{\text{PMP4}} = -2085.060582$	$E_{\text{PMP4}} = -2084.919634$
$E_{\text{QCISD}} = -2085.096762$	$E_{\text{QCISD}} = -2085.088418$	$E_{\text{QCISD}} = -2085.059293$	$E_{\text{QCISD}} = -2084.919858$
$E_{\text{QCISD(T)}} = -2085.099350$	$E_{\text{QCISD(T)}} = -2085.090607$	$E_{\text{QCISD(T)}} = -2085.061682$	$E_{\text{QCISD(T)}} = -2084.920658$
$T_{\text{ePMP2}} = 0.0$ eV	$T_{\text{ePMP2}} = 0.06$ eV	$T_{\text{ePMP2}} = 0.86$ eV	$I_{\text{aPMP2}} = 4.60$ eV
$T_{\text{ePMP3}} = 0.0$ eV	$T_{\text{ePMP3}} = 0.15$ eV	$T_{\text{ePMP3}} = 0.93$ eV	$I_{\text{aPMP3}} = 4.75$ eV
$T_{\text{ePMP4}} = 0.0$ eV	$T_{\text{ePMP4}} = 0.18$ eV	$T_{\text{ePMP4}} = 0.97$ eV	$I_{\text{aPMP4}} = 4.80$ eV
$T_{\text{eQCISD}} = 0.0$ eV	$T_{\text{eQCISD}} = 0.23$ eV	$T_{\text{eQCISD}} = 1.02$ eV	$I_{\text{aQCISD}} = 4.81$ eV
$T_{\text{eQCISD(T)}} = 0.0$ eV	$T_{\text{eQCISD(T)}} = 0.24$ eV	$T_{\text{eQCISD(T)}} = 1.02$ eV	$I_{\text{aQCISD(T)}} = 4.86$ eV

with ZPE correction at the QCISD/6-311 + G^{*} level).

The analogous low-spin $^1\Sigma^+$ ground states and low-lying $^3\Pi$, high-spin states were examined previously for LiAl and NaAl and found to yield almost the same 0.22 eV(LiAl) [9] and 0.23 eV (NaAl, both at QCISD(T)/6-311 + G(2df)) [2] excitation energies. To date, only LiB and NaB have been found to have $^3\Pi$, high-spin ground states among diatomics from the isoelectronic series AB, where A = H, Li, Na and B = B, Al, Ga.

4. Why is LiB a triplet and are LiAl and LiGa singlets?

It is natural to wonder why the ground states of LiB and NaB are triplets and those of LiAl, LiGa, NaAl and NaGa are singlets. To address this question, let us consider the electronic properties of the constituent atoms and of these molecules which are presented in Table 3.

From the Aufbau principle, one might expect singlet ground states with $1\sigma^2 2\sigma^2$ electronic configuration for all six molecules. The valence 1σ -MO is a bonding orbital with participation of atomic orbitals of both atoms, and the 2σ -MO is a lone pair of the group III atom. Because both MOs have σ -symmetry and are localized in similar regions of space, electrons occupying these MOs will strongly interact. As a result, the electrons in the 2σ -MO will be polarized away from the alkali atom. As noted in Table 3, the electron affinities of B, Al and Ga are very similar and are close to the electron affinity of Li, while the ionization potential of B is substantially higher than those of Al and Ga. Therefore, we believe, that it is the high IP of B that causes the triplet state ground states in LiB and NaB. That is, for LiB and NaB, electrons in the polarized 2σ -MO try to move far from the B center, which destabilizes the singlet state more than in LiAl, NaAl, LiGa. Promotion of one 2σ electron into the 1π -MO (which is composed almost completely from valence π -AOs of the group III atom) allows this electron to be closer to the nuclei. One can see from Table 3 that

Table 3
Calculated charge distributions in LiB, LiAl and LiGa^a

	LiB		LiAl		LiGa	
	$^1\Sigma^+$	$^3\Pi$	$^1\Sigma^+$	$^3\Pi$	$^1\Sigma^+$	$^3\Pi$
$R(\text{Li-M}), \text{\AA}$	2.419	2.141	2.847	2.623	2.874	2.637
$\Delta E, \text{kcal/mol}$	6.90	0.00	0.00	5.37	0.00	5.20
$Q^{\text{Mull}}(\text{M})^b$	+0.03	-0.30	+0.17	-0.15	-0.01	-0.40
$Q^{\text{Dipole}}(\text{M})^c$	-0.36	-0.61	-0.14	-0.38		
$Q^{\text{NBO}}(\text{M})^d$	-0.33	-0.74	-0.04	-0.54	-0.06	-0.55
μ_e, D	4.20	6.25	1.98	4.82	2.03	4.91
$\langle R^2 \rangle \text{ au}$	66.0	53.2	114.6	98.6	129.1	112.0
$\epsilon^{\text{HOMO}}, \text{eV}$	-5.49		-4.87		-4.85	
$\epsilon^{\text{LUMO}}, \text{eV}$	-0.19		+0.03		+0.03	
IP_a, eV	5.98	6.28	6.01	5.78	5.04	4.81
IP_M, eV^e	8.30		5.99		6.00	
$\text{IP}_{\text{Li}}, \text{eV}^e$	5.39		5.39		5.39	
EA_M, eV^f	0.28		0.44		0.30	
$\text{EA}_{\text{Li}}, \text{eV}^f$	0.62		0.62		0.62	

^a All data at QCISD/6-311 + G^{*}.

^b Effective charges calculated using Mulliken population analysis.

^c Effective charges were determined from a fit to the electrostatic potential at points selected according to the Merz–Singh–Kollman scheme and dipole moment (see Ref. [25] for details).

^d Effective charges calculated according natural population analysis (see Ref. [24] for details).

^e Data from Ref. [14].

^f Data from Ref. [13].

the charge distribution, measured by the mean value of $\langle R^2 \rangle$, is indeed more compact in the triplets than in the singlets. If one accepts this explanation, one can make a prediction that not only LiB and NaB have triplet ground states, but also KB, RbB and CsB, while the other AlkM molecules, where Alk = Li, Na, K, Rb and Cs and M = Al, Ga, In (IP = 5.79 eV) [14] and Tl (IP = 6.11 eV) [14] should have singlet ground states.

If one replaces the alkali atom by the valence isoelectronic hydrogen atom, one might expect, for example, that the singlet state in GaH will be even more stable than the triplet, because now the electrons in the 1σ -MO are polarized toward the hydrogen which makes it possible for the electrons in the 2σ -MO to remain near the Ga core, thus resulting in an increased relative stability of the singlet state. That is exactly what was found in recent ab initio calculations of the $^1\Sigma^+$ and $^3\Pi$ states of GaH by Kim and Balasubramanian [25], where the ground singlet electronic state was found to be more stable than the lowest triplet state by 48.1 kcal/mol. Taking this into account, one might expect that all HA (A = B, Al, Ga, In and Tl) must have singlet ground electronic states, which is exactly what was found experimentally for these molecules [26].

5. Ionization energies of LiGa and NaGa

We studied only the $^2\Sigma^+$ state of LiGa^+ and NaGa^+ , which we believe is the only candidate for the ground electronic state. Results of our calculations are also presented in Tables 1 and 2. For both cations, the bond length is longer and the vibrational frequency is lower than in the neutral molecules. The calculated ionization potentials for both LiGa and NaGa are lower than those of the constituent atoms, which reflects some antibonding character of the 2σ -HOMO, in agreement with our model above. The calculated dissociation energies of LiGa^+ and NaGa^+ were found to be $D_e(\text{LiGa}^+ \rightarrow \text{Li}^+ + \text{Ga}) = 27.1$ kcal/mol and $D_e(\text{NaGa}^+ \rightarrow \text{Na}^+ + \text{Ga}) = 19.2$ kcal/mol (all at QCISD(T)/6-311 + G(2df)). Both cations are somewhat more strongly bound than their neutral counterparts.

Acknowledgements

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