

# Electronic states and vibrational frequencies of the triatomic $\text{Ga}_2\text{N}$ , $\text{GaN}_2$ , and their cations and anions

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## Abstract

The low-lying electronic states of  $\text{Ga}_2\text{N}$ ,  $\text{GaN}_2$  and the corresponding anions and cations have been investigated using B3LYP, MP2, CCD, complete active space multi-configuration self-consistent field technique (CASSCF) and multi-reference singles + doubles configuration interaction (MRSDCI) calculations. Potential energy surfaces, geometries, energy separations, adiabatic ionization energies, electron affinities, vibrational frequencies, and dissociation energies are computed.

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## 1. Introduction

Group III nitrides are one of the most fascinating of the semiconducting materials due to their significant applications in blue and green light-emitting devices [1–3]. Such light-emitting diodes should find applications in flat-panel displays, and the related blue and ultraviolet laser diodes exhibit considerable promise for high-density optical data storage and high-resolution printing. Most of the past studies have dealt with the electronic and structural properties of solid-phase materials [4,5] and the process of chemical vapor deposition of GaN [6–9].

There are several experimental studies on three-atom and larger III–V clusters [10–16]. Neumark and coworkers [13–15] have studied the  $\text{Ga}_x\text{P}_y$  and their indium analogs using anion photodetachment spectroscopy. Among the smaller clusters, low-lying electronic states of  $\text{GaP}_2$ ,  $\text{Ga}_2\text{P}$ , and  $\text{Ga}_2\text{P}_3$  [13] as well as  $\text{In}_2\text{P}$  and  $\text{InP}_2$  [15] have been obtained. Zhou and Andrews [16]

have studied the reactions of laser-ablated gallium atoms with nitrogen atoms and molecules. They have obtained the vibrational spectra of small  $\text{Ga}_x\text{N}_y$  molecules including the trimers  $\text{Ga}_2\text{N}$  and  $\text{GaN}_2$ . There have been a few theoretical studies on small clusters containing Al and N, Ga and N and In and N [17–20] and related III–V clusters [21–27]. In the current work, we report the results of CASSCF, MRSDCI and other methods on the triatomic gallium nitride  $\text{Ga}_2\text{N}$  and  $\text{GaN}_2$  species and their ions. We have obtained the geometries and spectra and find that while different methods converged quite well for  $\text{Ga}_2\text{N}$ , there are conflicting results for  $\text{GaN}_2$ , which are explained on the basis of bonding.

## 2. Computational details

The electronic states of the  $\text{Ga}_2\text{N}$  molecule arises from the triplet ground state of  $\text{Ga}_2$  and the  $^4\text{S}$  state of N, resulting in doublet, quartet and sextet electronic states but the quartet and sextet states are likely to be considerably higher. We have calculated all the doublet

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states of Ga<sub>2</sub>N and some quartet states but found that the quartet states are considerably higher and unstable, and thus they were not considered further. Likewise although the triplet states were considered for the ions, the ground state of Ga<sub>2</sub>N<sup>+</sup> and Ga<sub>2</sub>N<sup>-</sup> were both found to be closed-shell <sup>1</sup>Σ<sub>g</sub><sup>+</sup> states.

All calculations were made with relativistic effective core potentials RECPS for the core electrons of Ga and N atoms with the outer 3d<sup>10</sup>4s<sup>2</sup>4p<sup>1</sup> shells for the Ga atom and the outer 2s<sup>2</sup>2p<sup>3</sup> for the N atom retained in the valence space, respectively. The RECPS and the valence GAUSSIAN basis sets for Ga have been employed before in other studies [21–25]. These basis sets were augmented with a set of six-component 3d functions with α = 0.8 for N. We have carried out DFT [28,29], MP2, CCSD and CASSCF/MRSDCI computations. In the CASSCF computations energetically lower 3d orbitals of the Ga atoms were kept inactive in that excitations from these orbitals were not allowed. The remaining valence 2s and 2p orbitals of N, and 3s and 3p orbitals of the Ga atoms were included in the active space. This resulted in an active space spanning six a<sub>1</sub>, three b<sub>2</sub>, three b<sub>1</sub> and zero a<sub>2</sub> orbitals, which we label 6330-CAS for Ga<sub>2</sub>N. Eleven electrons of Ga<sub>2</sub>N (10 for Ga<sub>2</sub>N cation and 12 for Ga<sub>2</sub>N anion) were distributed in all possible ways among these orbitals. The MRSDCI calculations included all configurations in the CASSCF with absolute coefficients ≥ 0.030 as reference configurations. Furthermore, multi-reference Davidson corrections (MRSDCI+Q) were calculated. The CASSCF/MRSDCI computations were carried out using one of the author's modified version of ALCHEMY II codes to include RECPS [30]. All other computations were made using GAUSSIAN '98 codes [31].

### 3. Results and discussion

Fig. 1 presents the bending potential energy curves for all of the doublet electronic states of Ga<sub>2</sub>N together with the <sup>1</sup>A<sub>1</sub> ground states of the cation and anion. For each of the Ga–N–Ga bond angles, the Ga–N bond lengths were optimized, and the minimum energy is plotted against bond angles in Fig. 1. All of the states of Ga<sub>2</sub>N and their ions form linear states as the lowest states, although some states have local bent minimum (e.g., <sup>2</sup>A<sub>2</sub>). Table 1 shows the optimized geometries and energy separations of these states at B3LYP, MP2, CCD, CASSCF, MRSDCI and MRSDCI+Q levels. As seen from Table 1 and Fig. 1, the <sup>2</sup>Σ<sub>u</sub><sup>+</sup>(<sup>2</sup>B<sub>2</sub>) state of Ga–N–Ga prevails as the ground state of Ga<sub>2</sub>N. Past work has shown that Ga<sub>2</sub> exhibits a bond length of 2.746 Å in its X<sup>0</sup><sub>u</sub><sup>-</sup>(<sup>3</sup>Π<sub>u</sub>) ground state originating from σ<sub>g</sub><sup>2</sup>σ<sub>u</sub><sup>2</sup>σ<sub>g</sub><sup>1</sup>π<sub>u</sub><sup>1</sup> [27]. The GaN diatomic exhibits a bond length of 2.06 Å in its <sup>3</sup>Σ<sup>-</sup> ground state originating from π<sup>2</sup>σ<sup>2</sup> [16]. We have calculated the bond

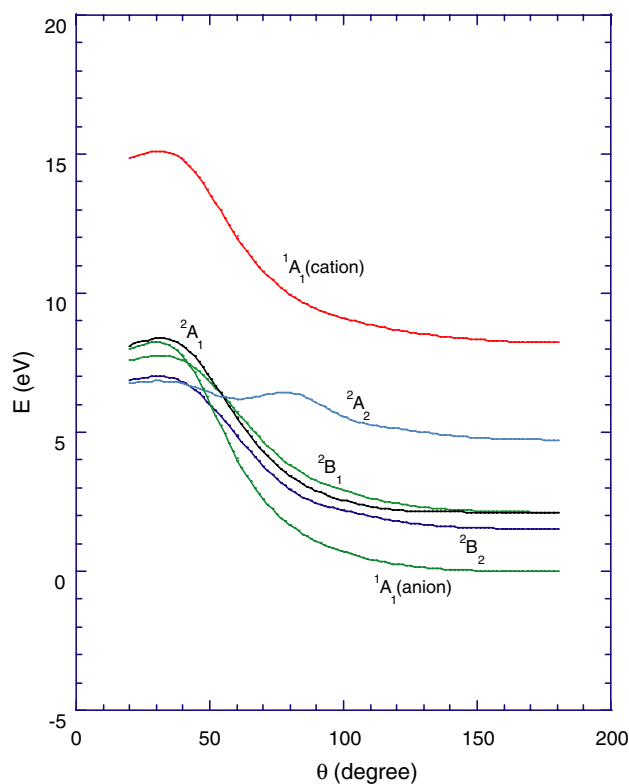


Fig. 1. Bending potential energy surfaces of Ga<sub>2</sub>N and the ions at CASSCF level.

length of GaN to be 2.013 and 1.951 Å at the B3LYP and MP2 levels, respectively, using our RECPS and basis sets. Thus our computed Ga–N bond distances of 1.725–1.778 Å suggest that Ga–N bonds are considerably stronger in Ga<sub>2</sub>N.

Unlike Ga<sub>2</sub>N, GaN<sub>2</sub> is considerably more difficult to treat due to the triple bond between the nitrogen atoms in N<sub>2</sub>. That is, the bonding in GaN<sub>2</sub> arises from the interaction of Ga<sup>+</sup> with N<sub>2</sub><sup>-</sup> through a process of electron donation and back transfer. Since the bonding tends to be weak, two nearly-degenerate electronic states are found for GaN<sub>2</sub> (Table 2). We have computed five minima at the B3LYP level but only four minima were located at the MP2 and CCD levels. We find that the linear Ga–N–N structure is the global minimum at all levels. However, there are sharp differences in the computed Ga–N bond distances between the DFT and MP2(CCSD) levels. This shows that the bonding between Ga and N<sub>2</sub> is weak and thus varies considerably with the levels of theory. We find the same features for the linear Ga–N–N<sup>-</sup> ground state in that B3LYP method predicts it to be lower than the ground state of neutral species but MP2 and CCD methods place the anion higher. This is not too surprising since the neutral species is not strongly bound. However, different levels of theory agree with each other for Ga–N–N<sup>+</sup> since the bonding is between Ga<sup>+</sup> and N<sub>2</sub> in this case, and it is somewhat stronger than the one between Ga and N<sub>2</sub>.

Table 1  
Geometries and energy separations for Ga<sub>2</sub>N, Ga<sub>2</sub>N<sup>+</sup>, and Ga<sub>2</sub>N<sup>-</sup>

		CASSCF	MRSDCI	MRSDCI+Q	B3LYP	MP2	CCD
<i>Ga<sub>2</sub>N</i>							
<sup>2</sup> Σ <sub>u</sub> <sup>+</sup>	<i>R</i> <sub>Ga–N</sub>	1.767			1.778	1.725	1.736
	<i>θ</i> <sub>Ga–N–Ga</sub>	180.0			180.0	180.0	180.0
	Δ <i>E</i>	0.00	0.00	0.00	0.00	0.00	0.00
<sup>2</sup> Π <sub>u</sub>	<i>R</i> <sub>Ga–N</sub>	1.889			1.913	1.866	1.865
	<i>θ</i> <sub>Ga–N–Ga</sub>	180.0			180.0	180.0	180.0
	Δ <i>E</i>	0.56	0.66	0.66	0.42	0.87	0.30
<sup>2</sup> Σ <sub>g</sub> <sup>+</sup>	<i>R</i> <sub>Ga–N</sub>	1.745			1.735	1.714	1.705
	<i>θ</i> <sub>Ga–N–Ga</sub>	180.0			180.0	180.0	180.0
	Δ <i>E</i>	3.20	3.28	3.25	2.10	2.03	2.07
<i>Ga<sub>2</sub>N<sup>+</sup></i>							
<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	<i>R</i> <sub>Ga–N</sub>	1.724			1.764	1.669	1.715
	<i>θ</i> <sub>Ga–N–Ga</sub>	180.0			180.0	180.0	180.0
	Δ <i>E</i>	6.71	7.29	7.38	7.98	7.43	7.60
<i>Ga<sub>2</sub>N<sup>-</sup></i>							
<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	<i>R</i> <sub>Ga–N</sub>	1.778			1.793	1.767	1.749
	<i>θ</i> <sub>Ga–N–Ga</sub>	180.0			180.0	180.0	180.0
	Δ <i>E</i>	-1.52	-1.72	-1.68	-1.99	-1.96	-1.80

\**R*<sub>c</sub> is in Å, *θ*<sub>c</sub> in degree, and Δ*E* in eV.

Table 2  
Geometries and energy separations for GaN<sub>2</sub>, GaN<sub>2</sub><sup>+</sup>, and GaN<sub>2</sub><sup>-</sup>

Molecule	Symmetry	State		B3LYP	MP2	CCD			
GaN <sub>2</sub>	C <sub>∞v</sub>	<sup>2</sup> Π	<i>R</i> <sub>Ga–N</sub>	2.316	2.865	2.900			
			<i>R</i> <sub>N–N</sub>	1.121	1.118	1.106			
			Δ <i>E</i>	0.00	0.00	0.00			
GaN <sub>2</sub>	C <sub>2v</sub>	<sup>2</sup> B <sub>2</sub>	<i>R</i> <sub>Ga–N</sub>	2.4525					
			<i>R</i> <sub>N–N</sub>	1.1407					
			<i>θ</i>	26.9					
			Δ <i>E</i>	0.07					
NGaN	C <sub>∞v</sub>	<sup>2</sup> Π	<i>R</i> <sub>Ga–N1</sub>	1.7689	1.728	1.6695			
			<i>R</i> <sub>Ga–N2</sub>	1.8848	1.7288	1.846			
			Δ <i>E</i>	5.96	6.73	6.29			
			<i>R</i> <sub>Ga–N</sub>	1.816	1.7286	1.710			
			Δ <i>E</i>	6.46	6.73	8.16			
	D <sub>∞h</sub>	<sup>4</sup> Π <sub>u</sub>	<i>R</i> <sub>Ga–N</sub>	1.8214	1.7605	1.7744			
			Δ <i>E</i>	5.82	6.95	6.35			
			NGaN <sup>+</sup>	D <sub>∞h</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	<i>R</i> <sub>Ga–N</sub>	1.791	1.8455	1.7883
						Δ <i>E</i>	18.58	19.32	17.71
						NGaN <sup>-</sup>	D <sub>∞h</sub>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	<i>R</i> <sub>Ga–N</sub>
Δ <i>E</i>	3.37	4.98	4.57						
GaN <sub>2</sub> <sup>+</sup>	C <sub>∞v</sub>	<sup>1</sup> Σ <sup>+</sup>	<i>R</i> <sub>Ga–N</sub>	2.7296	2.6987				2.7619
			<i>R</i> <sub>N–N</sub>	1.0992	1.1266	1.1063			
			Δ <i>E</i>	5.61	4.99	4.96			
GaN <sub>2</sub> <sup>-</sup>	C <sub>∞v</sub>	<sup>3</sup> Σ <sup>-</sup>	<i>R</i> <sub>Ga–N</sub>	2.0591	2.7639	2.7603			
			<i>R</i> <sub>N–N</sub>	1.1578	1.1097	1.1042			
			Δ <i>E</i>	-0.38	0.52	0.55			
			N <sub>2</sub> + Ga	0.22	0.10	0.08			
GaN + N	7.18	7.58	6.67						

\**R*<sub>c</sub> is in Å, *θ*<sub>c</sub> in degree, and Δ*E* in eV.

Table 3 shows the vibrational frequencies of Ga<sub>2</sub>N, GaN<sub>2</sub> and their ions at the DFT and CCD levels. There are good agreements for the states of Ga<sub>2</sub>N but somewhat less agreement is found for the states of GaN<sub>2</sub> presumably due to the weaker bonding in the case of GaN<sub>2</sub>.

Our computed results can be compared with previous experiment [16] and theory [16,17]. Both Zhou and Andrews [16] and Kandalam et al. [17] have computed <sup>2</sup>Σ<sub>u</sub><sup>+</sup> as the Ga–N–Ga ground state with Ga–N bond lengths of 1.788 and 1.79 Å, respectively in good agreement with our result of 1.778 and 1.736 Å at the B3LYP

Table 3  
Frequencies ( $\text{cm}^{-1}$ ) of  $\text{Ga}_2\text{N}$ ,  $\text{GaN}_2$ , and their ions

$\text{Ga}_x\text{N}_y$	symm	State	B3LYP				CCD			
			$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$
$\text{Ga}_2\text{N}$	$D_{\infty h}$	$^2\Sigma_u^+$	87.1	87.1	301.6	889.4	52.7	52.7	331.1	830.2
		$^2\Sigma_g^+$	272.7	272.7	354.5	1292.7				
$\text{Ga}_2\text{N}^+$	$D_{\infty h}$	$^1\Sigma_g^+$	152.9	152.9	302.9	866.0	136.7	136.7	332.8	945.5
$\text{Ga}_2\text{N}^-$	$D_{\infty h}$	$^1\Sigma_g^+$	61.7	61.7	304.6	989.8				
$\text{GaN}_2$	$C_{2v}$	$^2B_2$	126.6	275.4	1968.2					
$\text{NGaN}^a$	$C_{\infty v}$	$^2\Pi^a$	81.9	84.7	502.7	748.4				
	$D_{\infty h}$	$^2\Pi_g^a$	92.3	93.8	506.2	629.4				
$\text{NGaN}^+$	$D_{\infty h}$	$^1\Sigma_g^+$	80.4	80.4	647.9	803.7	111.9	111.9	620.3	966.1
$\text{NGaN}^-$	$D_{\infty h}$	$^3\Sigma_g^-$	102.5	102.5	680.8	708.9	189.5	189.5	726.3	736.2

<sup>a</sup> Small differences in the  $\omega_1$  and  $\omega_2$  frequencies of  $^2\Pi$  are due to symmetry breaking arising from computations done in  $C_{2h}$  or  $C_{2v}$  symmetries.

and CCD levels. However, we also find a  $^2\Pi_u$  and  $^2\Sigma_g^+$  excited states which have not been reported before. These states have positive frequencies at the B3LYP level. We have also computed the electron affinity of  $\text{Ga}_2\text{N}$  to be 1.7–2.0 eV for the first time. Our computed ionization energy of 7.98 eV at the DFT level agrees with the value of 8.18 eV computed by Kandalam et al. [17], but at higher levels we obtain lower values of 7.4–7.6 eV (Table 1). Our computed B3LYP vibrational frequencies for the ground state of  $\text{Ga}_2\text{N}$  agree quite well with those of Zhou and Andrews [16] at the same level, but our CCD results differ a bit as seen from Table 3. The experimental IR spectra of Zhou and Andrews [16] indicated a weak band at  $757.4 \text{ cm}^{-1}$  assigned to an asymmetric stretch and our CCD result of  $830.2 \text{ cm}^{-1}$  agrees somewhat better with this band than the B3LYP result, which suggests that higher level of theory with larger basis sets yield more satisfactory results.

The results of  $\text{GaN}_2$  are somewhat more conflicting in comparison to the previous works [16,17] due to the weaker Ga to  $\text{N}_2$  interaction. Zhou and Andrews [16] have suggested that the B3LYP method predicts a  $^4\Pi_u$  state as the ground state of  $\text{NGaN}$ . Unfortunately this state is computed by us at 5.82 eV higher than our  $\text{GaNN}^2\Pi$  ground state (B3LYP, Table 2). Our computed Ga–N bond lengths of 1.816 Å for the  $^4\Pi_u$  state agree with 1.821 Å obtained by Zhou and Andrews [16], but we disagree with the previous assignment [16] of this state to the ground state of  $\text{GaN}_2$ . Since the observed sharp bands at  $586.4$  and  $584.1 \text{ cm}^{-1}$  are attributed to the vibration of a single gallium atom, the only compatible vibrational mode among the states computed here is the asymmetric stretch of the  $^4\Pi_u$  state. However, this state is considerably higher in energy than the  $\text{GaNN}$  ground state. Consequently it is not clear as to how such a high-lying excited state could be formed with sufficient life time by the reaction of  $\text{GaN}$  with N, although  $^4\Pi_u$  is energetically

more stable than  $\text{GaN} + \text{N}$ . Moreover no experimental evidence is seen for the Ga–N–N ground state that we have computed here. Thus, more gas-phase experimental studies are warranted in view of this discrepancy.

In the case of  $\text{GaNN}$  Kandalam et al. [17] computed the Ga–N and N–N bond lengths to be 2.44 and 1.14 Å. Our results are similar at the B3LYP level but we differ significantly at the MP2 and CCD levels (Table 2). Moreover, Kandalam et al. [17] assign this linear structure not as a minimum, but with an imaginary frequency while we find all real frequencies at all levels (see Table 3). They find a very acute structure with an apex angle of 26 to be the minimum, where as we find a similar structure only at the DFT level to be at 0.07 eV above the linear structure. The bent structure is really a loose complex of Ga with  $\text{N}_2$  and has all real frequencies. The contrast between the B3LYP technique and the MP2(CCD) techniques is quite clear for  $\text{GaNN}$ ,  $\text{GaNN}^+$  and  $\text{GaNN}^-$  species (Table 2). The B3LYP method predicts much shorter Ga–N distance compared to the MP2 and CCD methods.

The nature of bonding in these species can be analyzed through the leading configurations and the Mulliken populations. The main component for the ground state  $^2\Sigma_u^+$  of  $\text{Ga}_2\text{N}$  is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^4$ , with coefficient 0.90. The main component for the  $^2\Pi_u$  state is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^3$ , with coefficient 0.93. The main components for the  $^2\Sigma_g^+$  state are  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^3 1\pi_g^1$ , with multiple coefficients of  $-0.81$  and  $0.34$ . The main components for the ground state  $^1\Sigma_g^+$  of the cation are  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4$  and  $1\sigma_g^2 1\sigma_u^2 2\sigma_u^1 1\pi_u^4$ , whose coefficients are 0.85 and 0.36, respectively, revealing multi-reference characters. This explains why the B3LYP result differs from MRSDCI+Q ionization energy. The main component for the ground state  $^1\Sigma_g^+$  of the anion is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^4$ , with a coefficient of 0.92. The differences between the doublet electronic states can be rationalized on the basis of the occupancies

Table 4  
Dissociation energies (eV)

	B3LYP	MP2	CCD	CCSD	CCSD(T)
Ga <sub>2</sub> N → GaN + Ga	4.23	5.04	4.10	4.25	4.59
Ga <sub>2</sub> N → Ga <sub>2</sub> + N	5.49	5.98	5.02	5.22	5.56
GaN → N + Ga	2.27	1.80	1.73	1.79	1.88
Ga <sub>2</sub> → Ga + Ga	1.02	0.86	0.81	0.82	0.90
GaNN → Ga + N <sub>2</sub>	0.22	0.10	0.08		
GaNN → GaN + N	7.18	7.58	6.67		
NGaN → Ga + N <sub>2</sub>	−5.60	−6.63	−6.21		
NGaN → GaN + N	1.36	0.85	0.38		
NGaN → NGaN <sup>+</sup>	12.76	12.59	11.42		
GaNN → GaNN <sup>+</sup>	5.61	4.99	4.96		

of the  $2\sigma_g$ ,  $2\sigma_u$ ,  $1\pi_u$ , and  $1\pi_g^1$  orbitals and their compositions. The  $2\sigma_g$  orbital is mainly made of Ga(s)–N(s) + Ga(s) whereas  $2\sigma_u$  is made of Ga(s)–N( $p_z$ )–Ga(s). The  $1\pi_u$  orbital is mainly composed of N( $p_y$ ) or N( $p_x$ ) with small contribution from of Ga( $p_y$ ) + Ga( $p_y$ ) or ( $p_x$ ). The  $1\pi_g^1$  orbital is mainly composed of Ga( $p_x$ )–Ga( $p_x$ ) or Ga( $p_y$ )–Ga( $p_y$ ). The  ${}^2\Pi_u$  state has a doubly-occupied  $2\sigma_u$ , while  $1\pi_u$  has three electrons. In contrast, in the  ${}^2\Sigma_u^+$  ground state,  $1\pi_u$  is fully occupied (four electrons) but  $2\sigma_u$  is half-filled. Both  ${}^2\Pi_u$  and  ${}^2\Sigma_u^+$  states have no electrons in  $1\pi_g$ . The closed-shell  ${}^1\Sigma_g^+$  state of the positive ion is formed from  ${}^2\Sigma_u^+$  by removing an electron from  $2\sigma_u$  (Ga(s)–N( $p_z$ )–Ga(s)). Consequently, removal of an electron from  $2\sigma_u$  results in the shortening of the Ga–N bonds. The Ga–N bond length of  ${}^1\Sigma_g^+$  is 1.724 Å, compared to 1.767 Å in the  ${}^2\Sigma_g^+$  state of Ga<sub>2</sub>N. Likewise addition of an electron to a slight anti-bonding orbital weakens the Ga–N bonds, and thus the Ga–N bond length of  ${}^1\Sigma_g^+$  state of the anion is 1.778 Å, compared to 1.767 Å for Ga<sub>2</sub>N.

The Mulliken populations of the electronic states for Ga<sub>2</sub>N and ions show that the gross populations of Ga are depleted by 0.45 for all of the doublet states of Ga<sub>2</sub>N, while the total N populations are enhanced by 0.9. The excess populations of 0.882–0.956 on N are evidently due to charge transfer from the Ga atoms to N leading to ionic Ga<sup>+</sup>N<sub>2</sub><sup>−</sup> bonding in Ga<sub>2</sub>N. The  ${}^2\Sigma_u^+$  ground state is composed of Ga(s<sup>1.634</sup>p<sup>0.911</sup>d<sup>9.978</sup>) and N(s<sup>1.716</sup>p<sup>4.211</sup>), while the gross populations for  ${}^2\Pi_u$  are Ga(s<sup>1.870</sup>p<sup>0.697</sup>d<sup>9.983</sup>) and N(s<sup>1.768</sup>p<sup>4.105</sup>). The primary difference in the populations between the two states arises from the s and p populations on the Ga atoms. The Ga(4s) population is 1.634 in  ${}^2\Sigma_u^+$ , which is obviously smaller than the corresponding population in  ${}^2\Pi_u$  (1.870), while the Ga(4p) population is 0.911 in  ${}^2\Sigma_u^+$ , which is noticeably larger than the corresponding population in  ${}^2\Pi_u$  (0.697). The Mulliken populations are consistent with the nature of the orbitals described earlier. We also note that Ga<sub>2</sub>N is found to be very different compared to the analogs such as Al<sub>2</sub>P, where the obtuse triangular minima rather than the linear structure are found [26]. The Mulliken populations of the Ga<sub>2</sub>N<sup>−</sup> ground state are Ga(s<sup>1.800</sup>p<sup>1.209</sup>d<sup>9.976</sup>) and

N(s<sup>1.699</sup>p<sup>4.296</sup>) compared to the Ga(s<sup>1.634</sup>p<sup>0.911</sup>d<sup>9.978</sup>) and N(s<sup>1.716</sup>p<sup>4.211</sup>) populations of the neutral  ${}^2\Sigma_u^+$  ground state. Since increase in the Ga population is 0.46/Ga, nearly all of the attached electronic density goes to each of Ga atoms. Neumark and coworkers [13,14] have obtained the electron affinity of the related Ga<sub>2</sub>P molecule as 2.507 eV.

Table 4 shows the results of the various dissociation energies at different levels of theories. We have computed the atomization energy for Ga<sub>2</sub>N in two steps, first, the dissociation energy  $D_e$  for Ga<sub>2</sub>N( ${}^2\Sigma_u^+$ ) → GaN( ${}^3\Sigma^-$ ) + Ga( ${}^2P$ ) is computed as 4.59 eV at CCSD(T) level. This was combined with the dissociation energy of GaN to yield the atomization energy of Ga<sub>2</sub>N as 6.47 eV. The bond dissociation energies of the Ga–Ga and Ga–N are 0.90 and 1.88 eV, respectively, at the CCSD(T) level (Table 4), indicating that the chemical bond of Ga–N is about 1.0 eV stronger than that of Ga–Ga. Ga<sub>2</sub>N can be readily formed either from GaN + Ga or from Ga<sub>2</sub> + N (Table 4).

As seen from Table 4, GaNN is bound by only 0.08–0.22 eV compared to Ga + N<sub>2</sub> at different levels of theory. In fact N–Ga–N is strongly unbound relative to Ga + N<sub>2</sub> by 5.6–6.21 eV. This structure is however bound relative to GaN + N and could thus be formed by the reaction of GaN with N. This is in agreement with the experimental results that NGaN spectra can only be observed under 30 K [16]. Table 4 also shows that the ionization energy of GaNN is about 7 eV lower than that of NGaN.

#### 4. Conclusion

We have computed the geometries, energy separations and vibrational spectra of Ga<sub>2</sub>N, GaN<sub>2</sub> and their ions using a number of methods such as B3LYP, MP2, CCSD and CASSCF/MRSDCI. Whereas the electronic states of Ga<sub>2</sub>N are predicted reasonably well by all of these techniques there are sharp differences in the computed properties of the electronic states of GaN<sub>2</sub> using the DFT method compared to other techniques due to the weakness of bonding between Ga



and  $N_2$ . Moreover, we find a substantially different ground state for  $GaN_2$  compared to the linear  $^4\Pi_u$  ground state reported before [16]. Our computed vibrational frequencies agree reasonably well with the experiment [16]. Although the experimentally observed bands of  $GaN_2$  near  $584\text{--}586\text{ cm}^{-1}$  agree with the asymmetric stretch of the  $^4\Pi_u$  state of  $NGaN$ , this state is considerably higher in energy. the  $^4\Pi_u$  state. However, this state is considerably higher in energy than the  $GaN$  ground state. Consequently it is not clear as to how such a high-lying excited state could be formed with sufficient life time by the reaction of  $GaN$  with  $N$ , although  $^4\Pi_u$  is energetically more stable than  $GaN + N$ . Since no experimental evidence is seen for the  $Ga\text{--}N\text{--}N$  ground state that we have computed here, more gas-phase experimental studies are warranted in view of this discrepancy. We have computed the ionization energies and electron affinities and the properties of a number of excited states of these species.

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