

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23182178>

# Theoretical Study of Gallium Nitride Molecules, GaN<sub>2</sub> and GaN<sub>4</sub>.

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · SEPTEMBER 2008

Impact Factor: 2.69 · DOI: 10.1021/jp8019396 · Source: PubMed

---

CITATION

1

---

READS

19

3 AUTHORS, INCLUDING:



Demeter Tzeli

National Hellenic Research Foundation

52 PUBLICATIONS 502 CITATIONS

SEE PROFILE



Ioannis D Petsalakis

National Hellenic Research Foundation

142 PUBLICATIONS 1,586 CITATIONS

SEE PROFILE

# Theoretical Study of Gallium Nitride Molecules, GaN<sub>2</sub> and GaN<sub>4</sub>.

Demeter Tzeli,\* Giannoula Theodorakopoulos, and Ioannis D. Petsalakis

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens GR-116 35, Greece

Received: March 5, 2008; Revised Manuscript Received: May 29, 2008

The electronic and geometric structures of gallium dinitride GaN<sub>2</sub>, and gallium tetranitride molecules, GaN<sub>4</sub>, were systematically studied by employing density functional theory and perturbation theory (MP2, MP4) in conjunction with the aug-cc-pVTZ basis set. In addition, for the ground-state of GaN<sub>4</sub>(<sup>2</sup>B<sub>1</sub>) a density functional theory study was carried out combining different functionals with different basis sets. A total of 7 minima have been identified for GaN<sub>2</sub>, while 37 structures were identified for GaN<sub>4</sub> corresponding to minima, transition states, and saddle points. We report geometries and dissociation energies for all the above structures as well as potential energy profiles, potential energy surfaces and bonding mechanisms for some low-lying electronic states of GaN<sub>4</sub>. The dissociation energy of the ground-state GaN<sub>2</sub>( $\tilde{X}^2\Pi$ ) is 1.1 kcal/mol with respect to Ga(<sup>2</sup>P) + N<sub>2</sub>( $X^1\Sigma_g^+$ ). The ground-state and the first two excited minima of GaN<sub>4</sub> are of <sup>2</sup>B<sub>1</sub>(C<sub>2v</sub>), <sup>2</sup>A<sub>1</sub>(C<sub>2v</sub>, five member ring), and <sup>4</sup> $\Sigma_g^-(D_{\infty h})$  symmetry, respectively. The dissociation energy (*D*<sub>e</sub>) of the ground-state of GaN<sub>4</sub>,  $\tilde{X}^2B_1$ , with respect to Ga(<sup>2</sup>P) + 2 N<sub>2</sub>( $X^1\Sigma_g^+$ ), is 2.4 kcal/mol, whereas the *D*<sub>e</sub> of <sup>4</sup> $\Sigma_g^-$  with respect to Ga(<sup>4</sup>P) + 2 N<sub>2</sub>( $X^1\Sigma_g^+$ ) is 17.6 kcal/mol.

## I. Introduction

Gallium nitrides are semiconducting materials with promising technological applications in microelectronics, nanomaterials, and optics.<sup>1–3</sup> Consequently a significant number of experimental and theoretical studies of the electronic, structural, and optical properties of the solid phase material have been reported in the literature.<sup>4</sup> Information on the geometry and electronic structure of small GaN clusters is essential for applications in microelectronics, yet work on such clusters either experimental or theoretical is less common, with publications of the latter kind being on the rise lately.

Several theoretical studies on Ga<sub>x</sub>N<sub>y</sub> species have been reported, for example on symmetric molecules, Ga<sub>n</sub>N<sub>n</sub> (*n* = 1–6<sup>5–8</sup>), but not many for the systems of interest here. For GaN<sub>2</sub> three previous studies exist: Kandalam et al.<sup>9</sup> employing density functional theory (DFT) calculations found 3 isomers. Zhou et al.<sup>10</sup> presented the spectra of laser-ablated Ga atoms codeposited with pure nitrogen and some DFT calculations where two states of GaN<sub>2</sub> were determined but not the ground state. In 2004, Wang et al.<sup>11</sup> using DFT, Møller–Plesset Perturbation theory (MP2) and Coupled-Clusters methods (CCD) calculated four isomers of the GaN<sub>2</sub> molecule. For the case of GaN<sub>4</sub>, there is only one study, where Song et al.<sup>12</sup> using the full potential linear muffin tin orbital method calculated three isomers. Thus, a comprehensive and systematic theoretical study of the possible stable structures of GaN<sub>2</sub> and GaN<sub>4</sub> were not pursued in these previous reports.

In the present work, which is a continuation of our previous work on the corresponding cations GaN<sub>2</sub><sup>+</sup> and GaN<sub>4</sub><sup>+</sup>,<sup>13</sup> gallium dinitride and tetranitride molecules, GaN<sub>2</sub> and GaN<sub>4</sub>, were systematically studied using both DFT and MP (MP2, MP4) techniques. In total, 7 minima for GaN<sub>2</sub> and 37 structures for GaN<sub>4</sub> were determined corresponding to minima, transition states, and saddle points. Total energies (*E*), binding energies (*D*<sub>e</sub>), and geometries (*r*<sub>e</sub>, angles) are reported for all 7 structures

of GaN<sub>2</sub> and for 17 of GaN<sub>4</sub>, while the corresponding data for the remaining 20 isomers (minima, transition states, and saddle points) calculated for GaN<sub>4</sub> are provided as Supporting Information. Moreover, vibrational frequencies, potential energy profiles (PEP), and two-dimensional sections of potential energy surfaces (PES) of some low-energy structures of GaN<sub>2</sub> and GaN<sub>4</sub> are plotted. Finally, the bonding process for selected structures is discussed.

In Section II, we describe the computational procedure followed, in Section III we discuss our results on the GaN<sub>2</sub> molecule, in Section IV our results on GaN<sub>4</sub>, and, finally, in Section V we present some conclusions and comments.

## II. Computational Procedure

For the GaN<sub>2</sub> molecule, the lowest lying, spin doublet and quartet, linear and bent (NNGa, NGaN) structures were calculated giving seven distinct species. For GaN<sub>4</sub>, a preliminary sampling of the configuration space and bonding networks was performed using the electronic structures of the combining fragments N<sub>4</sub> + Ga, N<sub>3</sub> + Ga + N, N<sub>2</sub> + GaN<sub>2</sub>, GaN<sub>3</sub> + N, and GaN<sub>2</sub> + 2N. About 80 structures were examined for stability resulting in 37 spin doublet and quartet geometry optimized electronic structures of GaN<sub>4</sub> at the B3LYP/LANL2DZ level of theory. B3LYP is a DFT functional using Becke's three parameter gradient corrected functional<sup>14</sup> with the gradient corrected correlation of Lee, Yang, and Parr.<sup>15</sup> The Hay-Wadt LANL2DZ ECP<sup>16</sup> basis set consists of a pseudopotential for the core electrons (up to 3d electrons) of Ga and a double- $\zeta$  quality basis set, for the three outer electrons of Ga, (4s<sup>2</sup>4p<sup>1</sup>), and the seven electrons of N, i.e., (3s3p) → [2s2p]<sub>Ga</sub> and (10s5p) → [3s2p]<sub>N</sub>. Moreover, additional calculations have been carried out for the ground-state of GaN<sub>4</sub> (<sup>2</sup>B<sub>1</sub>), which is a van der Waals isomer, in order to test the limits of reliability of the different theoretical procedures. The DFT method was used with various combinations involving 4 functionals [B3LYP,<sup>14,15</sup> B3PW91,<sup>17</sup> PBEPBE,<sup>18</sup> and LSDA<sup>19</sup>] and 10 basis sets [LANL2DZ,<sup>16</sup> DGDZVP,<sup>20</sup> cc-pVDZ,<sup>21</sup> SDD,<sup>22</sup> 6-311,<sup>23</sup>

\* Corresponding author. E-mail: dtzeli@eie.gr. Fax: +30-210-7273-794.

**TABLE 1: Absolute Energies  $E_e$  (h), Geometries  $r_{\text{Ga-N}}$ ,  $r_{\text{N-N}}$  (Å),  $\varphi$  (degrees), Dissociation Energies with Respect of Ga + 2N,  $D_{e1}$ (kcal/mol) and Ga + N<sub>2</sub>,  $D_{e2}$ (kcal/mol) and Relative Energy  $\Delta E$  (kcal/mol) of the GaN<sub>2</sub> Molecule**

method	$-E$	$r_{\text{Ga-N}}$	$r_{\text{N-N}}$	$\varphi$	$D_{e1}(\text{BSSE})^a$	$D_{e2}(\text{BSSE})^b$	$\Delta E$
<sup>2</sup> Ga-N-N(C <sub>∞v</sub> )				$\tilde{X}^2\Pi$			
B3LYP/LANL2DZ	111.510721	2.048	1.176	180.0	193.0(191.4)	11.68(8.04)	0.0
B3LYP/DGDZVP	2033.973475	2.447	1.121	180.0	220.7(219.9)	3.06(1.13)	0.0
B3LYP/6-311G+(2df)	2034.389912	2.742	1.097	180.0	230.4(229.4)	1.30(0.86)	0.0
MP2/6-311G+(2df)	2032.566167	3.321	1.113	180.0	231.2(227.7)	1.31(0.78)	0.0
MP2/cc-pVTZ	2032.724976	3.222	1.113	180.0	230.4(227.8)	1.61(0.91)	0.0
MP2/aug-cc-pVTZ	2032.735099	3.191	1.114	180.0	232.7(229.6)	2.10(1.03)	0.0
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.730154	3.301	1.115	180.0	(229.6)		0.0
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>d</sup>	2032.733445	3.306	1.114	180.0		(1.06)	0.0
MP4/aug-cc-pVTZ <sup>e</sup>	2032.776804				225.0(222.3)	2.01(0.99)	0.0
<sup>2</sup> N-Ga-N(C <sub>2v</sub> )				$I^2B_2$			
MP2/aug-cc-pVTZ	2032.733356	3.554	1.115	18.1	231.6(228.7)	1.00(0.13)	1.09
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.728827	3.845	1.116	16.7	(228.8)		0.83
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>d</sup>	2032.732149	3.879	1.115	16.5		(0.24)	0.81
<sup>4</sup> Ga-N-N(C <sub>∞v</sub> )				$\tilde{a}^4\Sigma^-$			
MP2/aug-cc-pVTZ	2032.619328	1.964	1.088	180.0	250.0(243.0)	19.4(14.5)	72.6
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.608174	2.000	1.088	180.0	(243.0)		76.5
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>d</sup>	2032.611433	2.002	1.087	180.0		(14.5)	76.6
<sup>4</sup> N-Ga-N(C <sub>2v</sub> )				$I^4A_2$			
MP2/aug-cc-pVTZ	2032.604600	2.216	1.143	29.9	240.8(234.6)	10.2(5.81)	81.9
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.594729	2.243	1.147	29.6	(234.6)		85.0
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>d</sup>	2032.597626	2.242	1.147	29.6		(5.81)	85.2
<sup>4</sup> N-Ga-N(C <sub>2v</sub> )				$I^4B_1$			
MP2/aug-cc-pVTZ	2032.578491	1.932	1.254	37.9	224.4(216.3)	-6.20(-13.0)	98.3
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.565594	1.948	1.257	37.6	(216.3)		103.3
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>d</sup>	2032.567832	1.948	1.257	37.6		(-12.9)	103.9
<sup>2</sup> N-Ga-N(D <sub>∞h</sub> )				$I^2\Pi_g$			
MP2/aug-cc-pVTZ	2032.486649	1.759	3.517	180.0	76.8(67.9)		155.9
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.472567	1.767	3.534	180.0	(68.0)		161.6
<sup>4</sup> N-Ga-N(D <sub>∞h</sub> )				$I^4\Pi_u$			
MP2/aug-cc-pVTZ	2032.470580	1.789	3.579	180.0	156.7(149.7)		166.0
MP2 <sub>BSSE</sub> /aug-cc-pVTZ <sup>c</sup>	2032.459488	1.796	3.592	180.0	(149.7)		169.8

<sup>a</sup>  $D_e$  values of doublet and quartet states calculated with respect to the Ga(<sup>2</sup>P) and Ga(<sup>4</sup>P) + 2N(<sup>4</sup>S), respectively. <sup>b</sup>  $D_e$  values of doublet and quartet states calculated with respect to the Ga(<sup>2</sup>P) and Ga(<sup>4</sup>P) + N<sub>2</sub>(<sup>1</sup> $\Sigma_g^+$ ), respectively. <sup>c</sup> MP2 optimized geometry for BSSE correction with respect to Ga + 2N. <sup>d</sup> MP2 optimized geometry for BSSE correction with respect to Ga + N<sub>2</sub>. <sup>e</sup> MP4/aug-cc-pVTZ//MP2/aug-cc-pVTZ.

6-311+<sup>23</sup> 6-311G(2df),<sup>23</sup> 6-311+G(2df),<sup>23</sup> 6-311+G(3df),<sup>23</sup> and aug-cc-pVTZ<sup>21</sup>]. Additionally, MP2 and MP4 calculations were carried out using the 6-311+G(2df),<sup>23</sup> cc-pVTZ,<sup>21</sup> and aug-cc-pVTZ<sup>21</sup> basis sets.

Subsequently, all 7 isomers of GaN<sub>2</sub> and the 17 lowest structures of GaN<sub>4</sub> were fully optimized at the unrestricted MP2/aug-cc-pVTZ level of theory, using second order perturbation theory and the augmented correlation-consistent basis of Dunning,<sup>21</sup> aug-cc-pVTZ (referred to as atz), i.e., (21s14p10d2f) → [7s6p4d2f]<sub>Ga</sub> and (11s6p3d2f) → [5s4p3d2f]<sub>N</sub>, thus involving 151(GaN<sub>2</sub>) and 243(GaN<sub>4</sub>) contracted Gaussian functions. The 3d<sup>10</sup>4s<sup>2</sup>4p<sup>1</sup> electrons of the Ga atom and the 2s<sup>2</sup>2p<sup>3</sup> electrons of the N atom have been correlated. As has been demonstrated previously for related systems (InN,<sup>24</sup> GaN,<sup>25</sup> Ga<sub>2</sub>N<sup>25</sup>), it is necessary to include the 3d<sup>10</sup> electrons in the valence set, for the calculation of geometries and dissociation energies. In order to evaluate the importance of the contribution of the third and fourth order of perturbation theory to the calculated quantities, single point MP4(SDTQ)/atz//MP2/atz calculations were carried out for the lowest minima of both GaN<sub>2</sub> and GaN<sub>4</sub>.

The harmonic frequencies of all 7 structures of GaN<sub>2</sub> and 37 of GaN<sub>4</sub> at DFT and MP2 level of theory were calculated so as to clarify whether they are minima or transition states and saddle points.

For all structures at all levels of theory, basis set superposition error (BSSE) corrections were made using the counterpoise procedure<sup>26,27</sup> since such corrections are especially important for van der Waals systems,<sup>28</sup> which is the case for most of the

structures calculated here. Furthermore, MP2 geometry optimizations were carried out with respect to the BSSE-corrected energy<sup>29</sup> (MP2<sub>BSSE</sub> calculations) for all 7 structures of GaN<sub>2</sub>.

Finally, it should be noted that there are no size nonextensivity problems in the plotting of the potential energy profiles of GaN<sub>2</sub> and GaN<sub>4</sub> with the relevant error being less than 7  $\mu$ h.

All the above DFT as well as MP calculations were performed using the Gaussian 03 program package.<sup>30</sup>

### III. GaN<sub>2</sub>

We have calculated seven linear and bent structures which all were minimum energy structures  $\tilde{X}^2\Pi$ ,  $I^2B_2$ ,  $\tilde{a}^4\Sigma^-$ ,  $I^4A_2$ ,  $I^4B_1$ ,  $I^2\Pi_g$ , and  $I^4\Pi_u$ , listed here in increasing total energy order. Their total energies ( $E$ ), geometries ( $r_e$ , angles), and dissociation energies with respect to the Ga(<sup>2</sup>P or <sup>4</sup>P) + 2N(<sup>4</sup>S) ( $D_{e1}$ ) and Ga(<sup>2</sup>P or <sup>4</sup>P) + N<sub>2</sub>(<sup>1</sup> $\Sigma_g^+$ ) ( $D_{e2}$ ), calculated with different computational procedures are presented in Table 1. The corresponding harmonic vibrational frequencies, IR intensities, and dipole moments at the MP2/atz level of theory are given in Table 2.

The three isomers of GaN<sub>2</sub> reported by Kandalam et al.<sup>9</sup> using the DFT (GGA/DNP) method, correspond to our  $\tilde{X}^2\Pi$ ,  $I^2B_2$ , and  $I^2\Pi_g$ , cf. Table 1, but they reported the  $I^2B_2$  isomer as the global minimum while their  $r_{\text{Ga-N}}$  distances were significantly smaller than our MP2/atz results, by up to 1 Å. Moreover, they reported a dissociation energy of 6.00 kcal/mol with respect to Ga + N<sub>2</sub> compared to our 1.06 kcal/mol (MP2<sub>BSSE</sub>/atz, see

**TABLE 2: GaN<sub>2</sub> Harmonic Frequencies  $\omega_e$  (cm<sup>-1</sup>), IR Intensities (km/mol), and Dipole Moments  $\mu$  (Debye) at the MP2/aug-cc-pVTZ Level of Theory**

	$\tilde{X}^2\Pi$		$I^2B_2$		$\tilde{a}^4\Sigma^-$		$I^4A_2$		$I^4B_1$		$I^2\Pi_g$		$I^4\Pi_u$	
	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR
$\omega_1$	42.2	0.12	31.8	0.17	281.6	54.9	372.3	87.9	202.0	0.51	269.0	765	114.1	49.6
$\omega_2$	49.6	0.06	49.7	0.03	347.2	1.22	593.1	32.2	548.7	28.4	760.6	0	333.3	3115
$\omega_3$	51.9	0.63	2173.7	1.3	347.2	1.22	2858.5	7759	3507.2	15868	990.8	380	535.9	1658
$\omega_4$	2285.8	3.9			3201.7	1591					6764.2		693.6	0
$\mu$	0.347		0.045		0.297		0.152		3.93		0		0	

below). As we will discuss below, the DFT method can give for some isomers of this molecule extremely small bond distances and large dissociation energies. In 2000, Zhou et al.<sup>10</sup> determined two isomers of GaN<sub>2</sub> ( $I^2\Pi_g$  and  $I^4\Pi_u$ ), again using DFT calculations. These isomers are found in the present work to lie 162 and 170 kcal/mol, respectively, above our global minimum. In 2004, Wang et al.<sup>11</sup> calculated the  $\tilde{X}^2\Pi$ ,  $I^2B_2$ ,  $I^2\Pi_g$ , and  $I^4\Pi_u$  isomers of the GaN<sub>2</sub> molecule, using a relativistic effective core potential in conjunction with a double- $\zeta$  quality basis set for the 3d4s4p electrons of Ga and 2s2p electrons of N and keeping the 3d electrons inactive. All four structures were calculated by DFT-B3LYP while three of them using the MP2 and CCD methods. They found for the global minimum a shorter  $r_{\text{Ga-N}}$  distance at their DFT level than to their MP2 and CCD. Furthermore, they found dissociation energies, with respect to Ga + N<sub>2</sub>, 5.01, 2.31, and 1.84 kcal/mol at the B3LYP, MP2, and CCD, respectively. As shown in Table 1, our results are in agreement with those of Wang et al.,<sup>11</sup> regarding the energy ordering of the above four structures. However, our  $r_{\text{Ga-N}}$  distance in  $\tilde{X}^2\Pi$  is larger than their MP2 and CCD values by 0.4 Å while our best result for the dissociation energy is 1.06 kcal/mol at MP2<sub>BSE</sub>/atz (see below). The differences are mainly due to the fact that our basis set is larger compared to theirs (augmented-triple- $\zeta$  vs double- $\zeta$ ) and second, due to the BSSE optimization carried out in the present calculations (see also below).

The ground-state of the GaN<sub>2</sub> molecule,  $\tilde{X}^2\Pi$ , is linear, consisting of a ground-state nitrogen molecule, N<sub>2</sub>( $X^1\Sigma_g^+$ ), interacting via a der Waals (vdW) bond with the Ga(<sup>2</sup>P) atom. Both natural and Mulliken population analyses show practically no charge transfer. Our best geometry at MP2<sub>BSE</sub>/atz (MP2/atz geometry which is optimized for the BSSE-corrected energy) level is  $r_{\text{Ga-N}} = 3.306$  and  $r_{\text{N-N}} = 1.114$  Å. The dissociation energy with respect to Ga + N<sub>2</sub>,  $D_{e2}$ , is 1.06 kcal/mol at the MP2<sub>BSE</sub>/atz level of theory. The MP4(SDTQ)/atz//MP2/atz dissociation energy is 1.0 kcal/mol, which is very close to the above MP2 value, suggesting that the MP2 method is sufficient. The spin contamination of the UMP2 calculation is very small with  $\langle S^2 \rangle = 0.753$  instead of 0.75. Comparing the ground-state of GaN<sub>2</sub> ( $\tilde{X}^2\Pi$ ) with that of the cation, GaN<sub>2</sub><sup>+</sup>( $\tilde{X}^1\Sigma^+$ ), they are both linear vdW species of the same type, where the neutral has a longer  $r_{\text{Ga-N}}$  bond by 0.5 Å and a smaller dissociation energy with respect to Ga + N<sub>2</sub> by 4 kcal/mol than the cation; see Table 1 and ref 13. Moreover, as in the case of the cation,<sup>13</sup> we observe that augmentation of the basis set with diffuse functions (aug-) results in a shorter vdW bond length compared with the same quality nonaugmented basis set while geometry optimization with respect to the BSSE-corrected energy results in a longer vdW bond length.

As in Wang et al.,<sup>11</sup> here too the DFT (B3LYP) method is found to give shorter vdW distances than the MP2 method. For example, it gives a bond length shorter by 1.14 using the LANL2DZ basis set, by 0.74 using the DGDZVP, and by 0.45 Å using the 6-311G+(2df) than the value of the MP2<sub>BSE</sub>/atz method. Moreover, the dissociation energy,  $D_{e2}$ , with respect

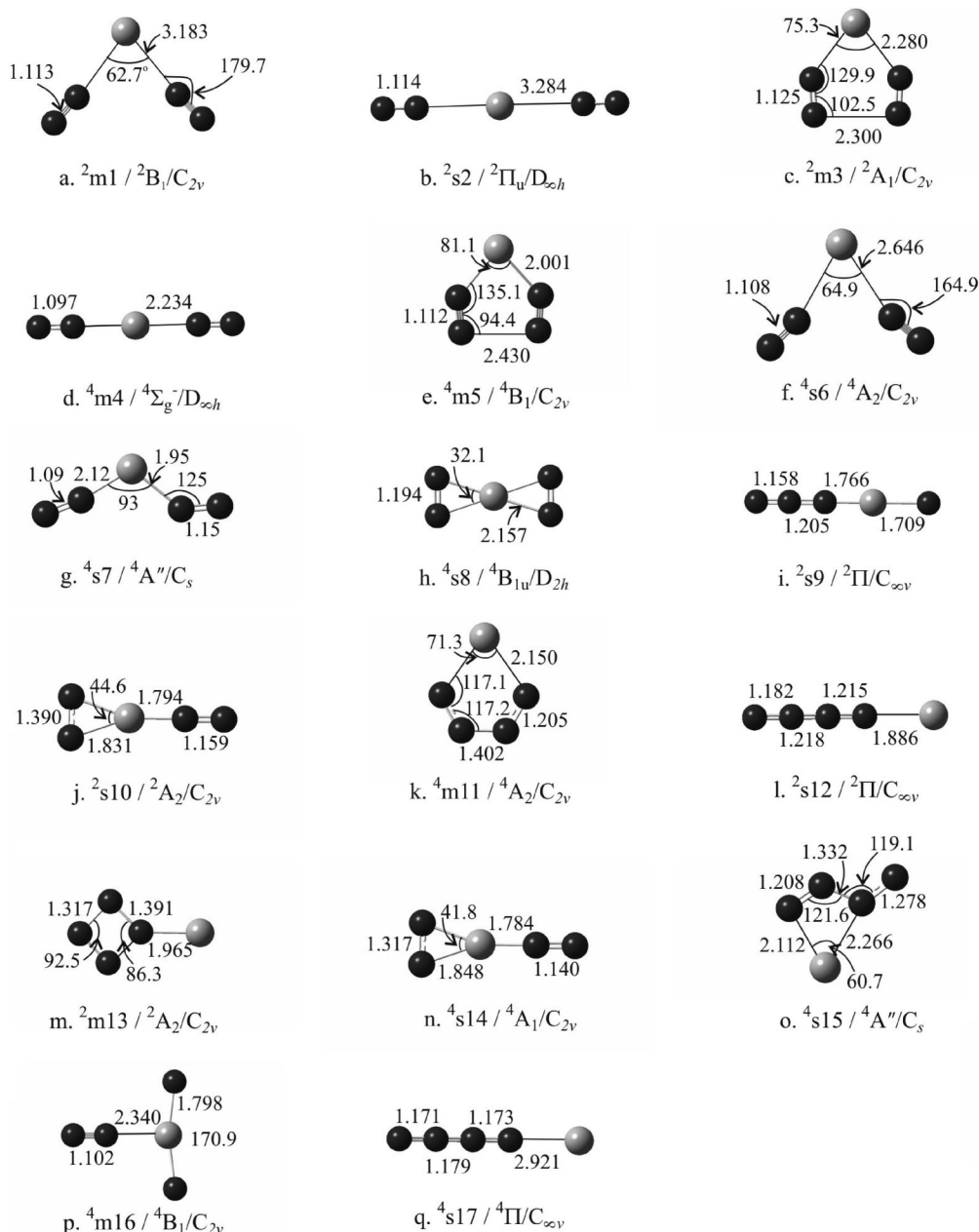
to Ga + N<sub>2</sub> is significantly overestimated for the LANL2DZ basis set ( $D_{e2} = 8.0$  kcal/mol), while DGDZVP gives 1.13 kcal/mol very close to the 1.06 kcal/mol of the MP2<sub>BSE</sub>/atz level of theory. However, the dissociation energy with respect to Ga + 2N is well described with the DFT methods (cf. Table 1).

The lowest energy bent structure of GaN<sub>2</sub>,  $I^2B_2$  is also a vdW structure with a Ga (<sup>2</sup>P) atom interacting with the triple bond of N<sub>2</sub>( $X^1\Sigma_g^+$ ) and forming a T-shaped molecule. This local minimum lies 0.8 kcal/mol above the global minimum at the MP2<sub>BSE</sub>/atz level of theory. Both the  $\tilde{X}^2\Pi$  and  $I^2B_2$  minima are on the same potential surface. The dissociation energy of  $I^2B_2$  ( $D_{e2}$ ) with respect to Ga + N<sub>2</sub> is only 0.24 kcal/mol, the distance between Ga and the middle of the N≡N triple bond is rather large at 3.839 Å, and the angle  $\varphi_{\text{NGaN}}$  is 16.7° at the MP2<sub>BSE</sub>/atz level of theory. Again the calculations show that there is practically no charge transfer between N≡N and Ga. Comparing the lowest bent structure of GaN<sub>2</sub>( $I^2B_2$ ) with that of GaN<sub>2</sub><sup>+</sup>( $I^1A_1$ ), they are both T-shaped vdW species of the same type where the neutral has a longer  $r_{\text{Ga-N}}$  bond by 0.4 Å and a smaller dissociation energy with respect to Ga+N<sub>2</sub> by 0.7 kcal/mol than the cation; see Table 1 and ref 13. The difference between these two lowest bent structures is that the  $I^2B_2$  isomer of GaN<sub>2</sub> is a minimum while the  $I^1A_1$  isomer of GaN<sub>2</sub><sup>+</sup> is a transition structure.

The first excited-state of GaN<sub>2</sub> calculated here is the linear  $\tilde{a}^4\Sigma^-$ , correlating with 2 N(<sup>4</sup>S) + Ga(<sup>4</sup>P) and N<sub>2</sub>( $X^1\Sigma_g^+$ ) + Ga(<sup>4</sup>P). The Ga atom is connected to N<sub>2</sub> with a  $\sigma$  interaction (which is formed between the empty 4p<sub>z</sub> orbital of Ga and the 2s<sup>2</sup> orbital of the adjacent N, where the first one gains about 0.2 e<sup>-</sup>) and two  $\pi$  interactions (between the 4p<sub>x</sub><sup>1</sup> orbital of Ga with the  $\pi_x$ <sup>2</sup> orbital of N<sub>2</sub> and the 4p<sub>y</sub><sup>1</sup> orbital of Ga and the  $\pi_y$ <sup>2</sup> orbital of N<sub>2</sub>). The natural population analysis for this structure gives Ga the following: 4s<sup>0.99</sup> 4p<sub>z</sub><sup>0.18</sup> 4p<sub>x</sub><sup>0.84</sup> 4p<sub>y</sub><sup>0.84</sup>. The middle N atom gains about 0.2 e<sup>-</sup>. The dissociation energy with respect to Ga(<sup>4</sup>P) + N<sub>2</sub>( $X^1\Sigma_g^+$ ) is 14.5 kcal/mol at MP2<sub>BSE</sub>/atz level of theory, and the vdW bond distance 2.002 Å at the same level. Thus the Ga-N bond length in the  $\tilde{a}^4\Sigma^-$  state of GaN<sub>2</sub> is shorter than the corresponding bond length of the ground-state by 1.3 Å (cf. Table 1). The spin contamination of the UMP2 calculation is very small with  $\langle S^2 \rangle = 3.80$  instead of 3.75.

The triangular  $I^4A_2$  and  $I^4B_1$  structures are minima, where Ga (<sup>4</sup>P) interacts with the ground-state N<sub>2</sub>( $X^1\Sigma_g^+$ ) and the excited-state N<sub>2</sub>( $a^3\Sigma_u^+$ ), respectively, as can be seen from the geometry and mainly by the population analysis and the orbitals. In the  $I^4A_2$  minimum the bond lengths are  $r_{\text{Ga-N}} = 2.242$  and  $r_{\text{N-N}} = 1.147$  Å at the MP2<sub>BSE</sub>/atz level of theory, see Table 1, and the dissociation energy with respect to Ga(<sup>4</sup>P) + N<sub>2</sub>( $X^1\Sigma_g^+$ ) is 5.81 kcal/mol. In the  $I^4B_1$  minimum the bond lengths are  $r_{\text{Ga-N}} = 1.948$  and  $r_{\text{N-N}} = 1.257$  Å at the MP2<sub>BSE</sub>/atz level of theory, see Table 1, which is close to the  $r_{\text{N-N}}$  distance in free N<sub>2</sub>( $a^3\Sigma_u^+$ ); here it is calculated as 1.2886 Å at the MP2/atz level of theory (expt: 1.2866 Å<sup>31</sup>). The  $a^3\Sigma_u^+$  state of N<sub>2</sub> is located 166.5 kcal/mol above the ground  $X^1\Sigma_g^+$  state at the MP2/atz level of theory. The  $I^4B_1$  state of GaN<sub>2</sub> is unbound with respect to Ga(<sup>4</sup>P) + N<sub>2</sub>( $X^1\Sigma_g^+$ ) (calculated  $D_{e2}$





**Figure 1.** Optimized geometries of 17 structures of doublet and quartet GaN<sub>4</sub> species at MP2/aug-cc-pVTZ level of theory, gray spheres = Ga, black spheres = N.

of  $-12.9$  kcal/mol), but it is bound with respect to  $Ga(^4P) + N_2(^3\Sigma_u^+)$  with a  $D_{e2}$  of 154 kcal/mol.

The frequency of the  $N\equiv N$  stretching mode is  $2186.2\text{ cm}^{-1}$  in the free  $N_2(X^1\Sigma_g^+)$  molecule at MP2/atx level. In the  $\tilde{X}^2\Pi$  and  $I^2B_2$  structures of GaN<sub>2</sub>, the corresponding frequencies are blue-shifted by 100 and red-shifted by  $12\text{ cm}^{-1}$ , respectively; see Table 2. Moreover, the  $\tilde{a}^4\Sigma^-$  structure exhibits a large blue shift of 1016 in this frequency, because the Ga–N bond is short and not a vdW bond, so the  $N_2$  moiety in GaN<sub>2</sub> is more rigid and cannot stretch freely. For the same reason the  $N-N$  stretching frequency of the  $I^4A_2$  structure shows a large blue shift of  $672\text{ cm}^{-1}$ . Similarly, the  $I^4B_1$  minimum which consists of  $Ga(^4P) + N_2(^3\Sigma_u^+)$ , presents a very large blue shift of 2052  $\text{cm}^{-1}$  in the  $N_2$  stretching frequency, compared to the corresponding frequency of  $1455.2\text{ cm}^{-1}$  of free  $N_2(^3\Sigma_u^+)$ .

The last two minima listed in Table 1,  $I^2\Pi_g$  and  $I^4\Pi_u$ , correspond to linear symmetric structures, N–Ga–N, with bond

distances  $r_{\text{Ga-N}} = 1.767$  and  $1.796\text{ \AA}$  at MP2<sub>BSSP</sub>/atx level, respectively. In both structures, the Ga atom is excited in the  $^4P$  state.

#### IV. GaN<sub>4</sub>

In the present work, we have calculated 37 structures, 16 minima, and 21 transition states or saddle points of the GaN<sub>4</sub> molecule. The results for the twenty highest-energy structures are given as Supporting Information. The geometries of the remaining 17 structures (7 minima and 10 transition states or saddle points) at the MP2/aug-cc-pVTZ level of theory are summarized in Figure 1. For convenience the structures have been labeled by three symbols the first (superscript) indicates the spin multiplicity (2 or 4), the second the kind of structure, i.e., whether it is a minimum (m) or a saddle point (s) and the third the energy rank of the structure, for instance  ${}^2m3$  means 2 = doublet, m = minimum and 3 = third lowest energy

**TABLE 3: Absolute Energies  $E_e$  (hartree), Dissociation Energies and BSSE-corrected Values  $D_e$ (BSSE) (kcal/mol), and Geometries  $r_{\text{Ga-N}}$ ,  $r_{\text{N-N}}$  (Å),  $\varphi_{\text{NGaN}}$ ,  $\varphi_{\text{GaNN}}$  (degrees) at Different Levels of Theory for the Ground State of  $\text{GaN}_4$ ,  ${}^2\text{m1}(\tilde{X}^2\text{B}_1)$ , and  ${}^2\text{s2}({}^2\Pi_u)$  Structures**

Method	$-E_e$	$D_{e1}(\text{BSSE})$ $\text{GaN}_4 \rightarrow \text{Ga} + 4\text{N}$	$D_{e2}(\text{BSSE})$ $\text{GaN}_4 \rightarrow \text{Ga} + 2\text{N}_2$	$D_{e3}(\text{BSSE})$ $\text{GaN}_4 \rightarrow \text{GaN}_2 + \text{N}_2$	$r_{\text{Ga-N}}$	$r_{\text{N-N}}$	$\varphi_{\text{NGaN}}$	$\varphi_{\text{GaNN}}$
${}^2\text{m1}(\tilde{X}^2\text{B}_1)$								
B3LYP/LANL2DZ	221.000832	380.0(377.4)	17.49(10.17)	5.81(1.83)	2.194	1.152	75.0	165.0
B3LYP/DGDZVP	2143.513989	441.3(439.9)	6.08(2.51)	3.02(1.12)	2.572	1.116	71.3	170.3
B3LYP/cc-pVDZ	2143.907398	451.7(446.6)	6.03(2.19)	3.03(1.01)	2.575	1.111	71.8	168.5
B3LYP/SDD	221.027985	377.2(374.5)	14.67(7.80)	5.50(1.82)	2.321	1.150	73.2	168.5
B3PW91/DGDZVP	2143.371876	434.4(432.9)	4.57(1.30)	2.31(0.56)	2.536	1.114	71.7	168.5
PBEPBE/DGDZVP	2142.951939	480.6(478.6)	14.35(9.75)	6.33(3.88)	2.366	1.134	72.9	164.9
LSDA/DGDZVP	2139.939591	555.9(553.6)	31.47(25.79)	14.63(11.57)	2.163	1.132	73.8	160.3
B3LYP/6-311	2143.828287	397.0(389.5)	13.63(5.71)	4.90(0.92)	2.299	1.132	74.1	168.8
B3LYP/6-311+	2143.836189	390.3(383.5)	7.20(0.44)	4.34(1.18)	2.311	1.132	74.0	167.8
B3LYP/6-311G(2df)	2143.953811	463.3(459.8)	4.23(1.84)	2.17(0.94)	2.685	1.096	71.4	170.0
B3LYP/6-311+G(2df)	2143.958472	460.7(459.0)	2.60(1.84)	1.30(0.93)	2.767	1.096	71.5	173.5
B3LYP/6-311+G(3df)	2143.963503	461.7(459.5)	2.49(1.93)	1.25(0.98)	2.793	1.096	71.6	173.7
B3LYP/aug-cc-pVTZ	2144.042288	460.1(459.3)	3.91(3.44)	1.98(1.79)	2.737	1.096	72.0	171.2
MP2/6-311+G(2df)	2141.921128	462.7(455.7)	3.01(1.91)	1.70(1.04)	3.288	1.113	60.8	176.0
MP2/cc-pVTZ	2142.085853	461.1(455.9)	3.56(2.03)	1.96(1.11)	3.186	1.113	62.4	175.3
MP2/aug-cc-pVTZ	2142.104298	466.1(459.6)	4.86(2.43)	2.76(1.39)	3.183	1.113	62.7	179.7
MP4/aug-cc-pVTZ	2142.168235	450.7(445.0)	4.60(2.28)	2.59(1.27)				
${}^2\text{s2}({}^2\Pi_u)$								
B3LYP/LANL2DZ	220.986049	370.8(368.4)	8.21(3.52)	3.47(0.91)	2.734	1.140	180.0	180.0
MP2/6-311+G(2df)	2141.920484	462.3(455.3)	2.60(1.52)	1.29(0.80)	3.359	1.113	180.0	180.0
MP2/cc-pVTZ	2142.085142	460.6(455.6)	3.12(1.74)	1.51(0.83)	3.285	1.113	180.0	180.0
MP2/aug-cc-pVTZ	2142.102550	465.0(459.1)	3.76(2.01)	1.66(1.00)	3.284	1.114	180.0	180.0
MP4/aug-cc-pVTZ	2142.166705	449.9(444.8)	3.64(1.94)	1.63(0.97)				

**TABLE 4:  $\text{GaN}_4$  Structures Absolute Energies  $E_e$  (hartree), Dissociation Energies and BSSE-corrected Values  $D_e$ (BSSE) (kcal/mol), Dipole Moments  $\mu$  (Debye), and Energy Differences  $\Delta E$  (kcal/mol) at MP2[MP4]/aug-cc-pVTZ Level of Theory**

struct	$-E_e$	$D_{e1}(\text{BSSE})^a$ $\text{GaN}_4 \rightarrow \text{Ga} + 4\text{N}$	$D_{e2}(\text{BSSE})^b$ $\text{GaN}_4 \rightarrow \text{Ga} + 2\text{N}_2$	$D_{e3}(\text{BSSE})^c$ $\text{GaN}_4 \rightarrow \text{GaN}_2 + \text{N}_2$	$D_{e4}(\text{BSSE})^d$ $\text{GaN}_4 \rightarrow \text{Ga} + \text{N}_4$	$\mu$	$\Delta E$
${}^2\text{m1}$	2142.104298 [2142.168235]	466.1(459.6) [450.7(445.0)]	4.86(2.43) [4.60(2.28)]	2.76(1.39) [2.59(1.27)]		0.57	0.0 [0.0]
${}^2\text{s2}$	2142.102550 [2142.166705]	465.0(459.1) [449.9(444.8)]	3.76(2.01) [3.64(1.94)]	1.66(1.00) [1.63(0.97)]		0.0	1.1 [1.0]
${}^2\text{m3}$	2142.073086	446.5(434.4)			148.3(140.6)	2.91	19.6
${}^4\text{m4}$	2141.991615	485.4(474.8)	24.12(17.58)	4.70(1.91)		0.0	70.7
${}^4\text{m5}$	2141.969174	471.3(457.1)	10.04(−0.45)			2.46	84.8
${}^4\text{s6}$	2141.962972	467.4(459.5)	6.15(2.25)			1.49	88.7
${}^4\text{s7}$	2141.958692	464.7(451.0)	3.47(−6.51)			4.05	91.4
${}^4\text{s8}$	2141.927337	445.0(433.6)				0.0	111.0
${}^2\text{s9}$	2141.916270	348.1(332.9)				3.83	118.0
${}^2\text{s10}$	2141.890270	331.8(315.1)				4.07	134.3
${}^4\text{m11}$	2141.889402	331.2(317.6) <sup>e</sup>			48.6(41.0)	1.61	134.8
${}^2\text{s12}$	2141.880288	325.5(312.2)			62.5(54.8)	3.39	140.6
${}^2\text{m13}$	2141.873578	321.3(309.1)			74.8(67.9)	4.62	144.8
${}^4\text{s14}$	2141.865259	406.1(391.6)				2.57	150.0
${}^4\text{s15}$	2141.864245	315.4(302.3) <sup>e</sup>			53.3(44.9)	3.41	150.6
${}^4\text{m16}$	2141.848101	395.3(382.3)				1.14	160.8
${}^4\text{s17}$	2141.784659	265.5(257.6) <sup>e</sup>			3.33(1.45)	1.16	200.6

<sup>a</sup>  $D_e$  with respect to  $\text{Ga}({}^2\text{P}$  and  ${}^4\text{P}) + 4\text{N}({}^4\text{S})$  for the doublet and quartet states, respectively. <sup>b</sup>  $D_e$  with respect to  $\text{Ga}({}^2\text{P}$  and  ${}^4\text{P}) + 2\text{N}_2$  ( $X^1\Sigma_g^+$ ) for the doublet and quartet states, respectively. <sup>c</sup>  $D_e$  with respect to  $\text{GaN}_2(\tilde{X}^2\Pi$  and  $\tilde{a}^4\Sigma^-) + \text{N}_2$  ( $X^1\Sigma_g^+$ ) for the doublet and quartet states, respectively. <sup>d</sup>  $D_e$  with respect to  $\text{Ga}({}^2\text{P}) + \text{rectangular cyclic } \text{N}_4({}^3\text{B}_2)$  for  ${}^2\text{m3}$ ,  $\text{Ga}({}^2\text{P}) + \text{trapezoid } \text{N}_4({}^3\text{B}_2)$  for  ${}^2\text{m11}$ ,  $\text{Ga}({}^2\text{P}) + \text{linear } \text{N}_4({}^1\Sigma)$  for  ${}^2\text{s12}$ ,  $\text{Ga}({}^2\text{P}) + \text{rhombic } \text{N}_4({}^3\text{B}_2)$  for  ${}^2\text{m13}$ , and  $\text{Ga}({}^2\text{P}) + \text{N}_4({}^3\Sigma)$  for  ${}^4\text{s15}$  and  ${}^4\text{s17}$ . <sup>e</sup>  $D_e$  with respect to  $\text{Ga}({}^2\text{P}) + 4\text{N}({}^4\text{S})$ . With respect to  $\text{Ga}({}^4\text{P}) + 4\text{N}({}^4\text{S})$  is 421.2(408.7) for  ${}^4\text{m11}$ , 405.4 (393.4) for  ${}^4\text{s15}$ , and 355.5(347.8) kcal/mol for  ${}^4\text{s17}$ .

structure. The results of a DFT study of the  ${}^2\text{m1}$  and  ${}^2\text{s2}$  structures are presented in Table 3, while for all 17 structures presented here, total energies ( $E$ ), dissociation energies  $D_{e1}$  with respect to  $\text{Ga}({}^2\text{P}$  or  ${}^4\text{P}) + 4\text{N}({}^4\text{S})$ ,  $D_{e2}$  with respect to  $\text{Ga}({}^2\text{P}$  or  ${}^4\text{P}) + 2\text{N}_2(X^1\Sigma_g^+)$ ,  $D_{e3}$  with respect to  $\text{GaN}_2(\tilde{X}^2\Pi$  or  $\tilde{a}^4\Sigma^-) + \text{N}_2(X^1\Sigma_g^+)$ , and  $D_{e4}$  with respect to  $\text{Ga} + \text{N}_4$  (optimized structures of  $\text{N}_4$  molecule) as appropriate in each case (see discussion below) and dipole moments are presented in Table 4. Furthermore, their vibrational frequencies and IR intensities are given in Table 5. Figures 2–6 depict the optimized potential energy

profiles with respect to  $\text{Ga} + 2\text{N}_2$  or  $\text{GaN}_2 + \text{N}_2$ , the optimized potential energy curves, and two-dimensional potential energy surfaces of the lowest doublet and quartet minima.

The ground-state of  $\text{GaN}_4$ ,  $\tilde{X}^2\text{B}_1$ , is a triangular structure (Figure 1a,  ${}^2\text{m1}$ ), as was in the case of the  $\text{GaN}_4^+$  cation,  $\tilde{X}^1\text{A}_1$ .<sup>13</sup> The  $\tilde{X}^2\text{B}_1$  structure of  $\text{GaN}_4$  may be considered as either having two  $\text{N}_2(X^1\Sigma_g^+)$  interacting with  $\text{Ga}({}^2\text{P})$  via two van der Waals (vdW) bonds which form an angle  $\varphi_{\text{NGaN}} = 62.7^\circ$  (MP2/atz level of theory) or having one  $\text{GaN}_2(\tilde{X}^2\Pi)$  interacting with a  $\text{N}_2(X^1\Sigma_g^+)$ . The bond lengths  $r_{\text{N-N}}$  and  $r_{\text{Ga-N}}$  are similar to the

**TABLE 5: Harmonic Frequencies (cm<sup>-1</sup>) and IR Intensities (km/mol) of the Seven Doublet and Eight Quartet Structures of the GaN<sub>4</sub> Molecule at MP2/cc-pVTZ and MP2/aug-cc-pVTZ Level of Theory**

	<sup>2</sup> m1				<sup>2</sup> s2				<sup>2</sup> m3		<sup>4</sup> m4	
	cc-pVTZ		aug-cc-pVTZ		cc-pVTZ		aug-cc-pVTZ		aug-cc-pVTZ		aug-cc-pVTZ	
	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR
$\omega_1$	20.1	0.02	25.5	0.04	5.8	0.04	14.6i	0.06	203.3	14.0	49.5	0.20
$\omega_2$	31.4	0.15	38.6	0.19	13.6	0.01	10.1	0.02	204.9	28.4	49.5	0.20
$\omega_3$	46.1	0	45.9	~0	34.9	0	38.3	0.20	269.6	4.4	84.2	0.25
$\omega_4$	49.1	0.17	49.1	0.14	35.7	0.24	39.9	0.0001	272.0	0.04	187.0	0
$\omega_5$	54.5	0.18	54.9	0.12	39.2	0	44.3	0	373.3	0.04	224.5	0
$\omega_6$	59.9	0.91	57.8	0.86	48.1	0	44.9	0	447.1	2.7	224.5	0
$\omega_7$	73.5	0	86.0	0.04	57.3	1.5	51.6	1.2	1456	970086	298.6	0.88
$\omega_8$	2292	4.2	2330	12.4	80.1	0.44	80.4	0.41	2876	4270	298.6	0.88
$\omega_9$	2293	1.3	2331	3.8	2252	0	2249	0.002	3891	6347	3457	0
$\omega_{10}$					2252	1.9	2249	2.8			3583	1175

	<sup>4</sup> m5		<sup>4</sup> s6		<sup>4</sup> s8		<sup>2</sup> s9		<sup>2</sup> s10	
	aug-cc-pVTZ		aug-cc-pVTZ		aug-cc-pVTZ		cc-pVTZ		aug-cc-pVTZ	
	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR
$\omega_1$	200.9	0.07	212.2i	0.04	282.1i	0	142.9i	1.9	154.6i	5.0
$\omega_2$	305.3	0.49	62.6	0.78	144.5i	1.83	111.7i	0	115.5i	0.09
$\omega_3$	314.6	14.6	76.6	4.6	110.5	1353	142.3	60.2	124.1	60.1
$\omega_4$	352.1	151	109.5	0.60	351.7	0	487.0	13.6	480.8	13.8
$\omega_5$	356.8	0	125.5	0	364.0	141	532.0	166	514.2	206
$\omega_6$	471.3	212	141.8	0.07	419.1	0	568.1	5.3	554.8	3.3
$\omega_7$	521.9	18.4	243.9	2.01	461.7	38.7	810.9	5614	747.9	4219
$\omega_8$	3140	330	2980	349	1606	716	1132	2853	1121	2794
$\omega_9$	5032	203480	3025	395	1723	0	1574	451	1572	400
$\omega_{10}$							2472	288	2453	173

	<sup>2</sup> s10		<sup>4</sup> m11		<sup>2</sup> s12		<sup>2</sup> m13		<sup>4</sup> s14	
	aug-cc-pVTZ		aug-cc-pVTZ		cc-pVTZ		aug-cc-pVTZ		aug-cc-pVTZ	
	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR	$\omega_e$	IR
$\omega_1$	19.9i	21.9	174.2	4.2	868.5i	4.5	846.8i	4.4	70.1	0.34
$\omega_2$	93.4	31.0	205.2	7.1	477.8i	5.6	437.3i	8.5	74.2	3.3
$\omega_3$	296.4	4.8	334.7	61.5	302.5i	10.1	288.8i	13.0	306.3	71.9
$\omega_4$	306.3	3.4	421.6	37.6	8.32i	1.07	56.3	1.7	402.4	14.1
$\omega_5$	521.1	2.8	536.9	0	57.4i	1.08	79.3	1.6	416.0	1.33
$\omega_6$	606.9	2.7	703.8	620	355.6	96.5	345.1	108	744.0	0.02
$\omega_7$	802.1	395	771.5	26.7	461.5	12.7	463.0	12.0	992.7	518
$\omega_8$	1144	545	1561	382	1221	873	1216	971	1221	40032
$\omega_9$	2062	6.02	2656	20149	1826	5.0	1802	0.81	1431	23.3
$\omega_{10}$					3810	6263	3804	6207		

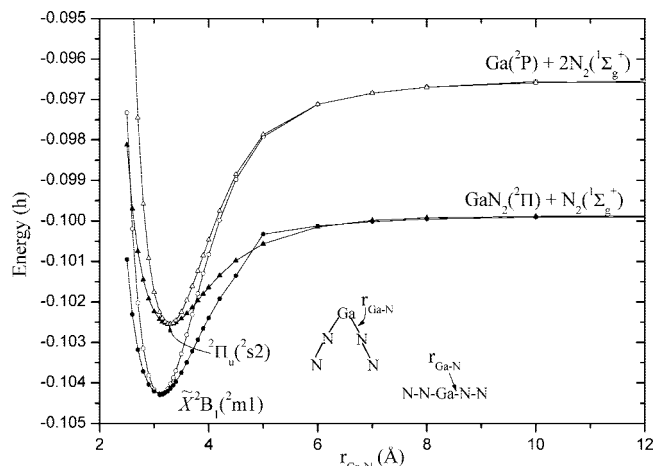
	<sup>4</sup> s15		<sup>4</sup> m16	
	aug-cc-pVTZ		aug-cc-pVTZ	
	$\omega_e$	IR	$\omega_e$	IR
$\omega_1$	68.71i	2.8	50.5	1.8
$\omega_2$	172.9	30.2	119.0	6.0
$\omega_3$	293.5	25.0	153.7	37.9
$\omega_4$	319.5	0.84	169.1	46.2
$\omega_5$	358.6	34.0	200.6	21.2
$\omega_6$	665.8	16.3	300.0	169
$\omega_7$	1086	44.3	525.0	1470
$\omega_8$	1129	79.2	684.4	0.002
$\omega_9$	1556	133	3209	438

corresponding values in GaN<sub>2</sub> ( $\tilde{X}^2\Pi$ ) at all levels of theory (cf. Tables 1 and 3). It is expected that in this case, as well as in all structures of GaN<sub>4</sub> calculated here, the bond lengths are slightly underestimated since it is not practical to carry out optimizations with respect to the BSSE-corrected energy. As shown in Table 1, this omission leads to an underestimation of the Ga–N bond length in the ground-state of GaN<sub>2</sub> by 0.1 Å.

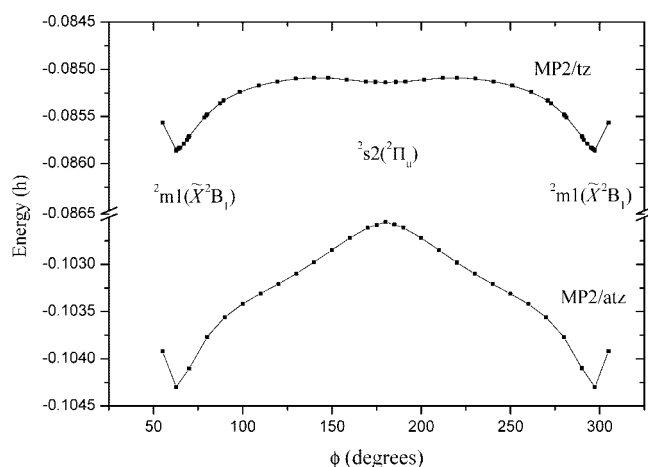
It might be noted that the cation has a shorter  $r_{\text{Ga-N}}$  bond length by ~0.5 Å, a larger angle by 9°, and a larger  $D_{\text{e3}}$  with respect to GaN<sub>2</sub><sup>(+)</sup> + N<sub>2</sub> by 3.5 kcal/mol than the neutral

molecule.<sup>13</sup> Natural population analysis shows practically no charge transfer in the molecule. The spin contamination of the UMP2 calculation is very small with  $\langle S^2 \rangle = 0.755$  instead of 0.75.

The results of DFT calculations on <sup>2</sup>m1 and on the corresponding linear <sup>2</sup>s2 structure are presented in Table 3, i.e., total energies ( $E$ ), dissociation energies  $D_{\text{e1}}$  with respect to Ga(<sup>2</sup>P) + 4N(<sup>4</sup>S),  $D_{\text{e2}}$  with respect to Ga(<sup>2</sup>P) + 2N<sub>2</sub>( $X^1\Sigma_g^+$ ), and  $D_{\text{e3}}$  with respect to GaN<sub>2</sub>( $\tilde{X}^2\Pi$ ) + N<sub>2</sub>( $X^1\Sigma_g^+$ ) and geometries. A series of four functionals, i.e., B3LYP, B3PW91, PBEPBE and



**Figure 2.** Potential energy curves of the  ${}^2m1(\tilde{X}^2B_1)$  and  ${}^2s2({}^2\Pi_u)$  isomers of the  $GaN_4$  molecule with respect to the  $r_{Ga-N}$  distance at the MP2/aug-cc-pVTZ level of theory. All energies shifted by +2142.0 h.



**Figure 3.** Optimized potential energy profiles  ${}^2m1(\tilde{X}^2B_1)$ – ${}^2s2({}^2\Pi_u)$ – ${}^2m1(\tilde{X}^2B_1)$  of the  $GaN_4$  molecule with respect to the  $\phi$  angle. All energies shifted by +2142.0 h.

LSDA and ten basis sets, namely, LANL2DZ, DGDZVP, cc-pVDZ, SDD, 6-311, 6-311+, 6-311G(2df), 6-311+G(2df), 6-311+G(3df), and aug-cc-pVTZ have been employed in different combinations. Additional MP2 and MP4 results were carried out using the 6-311+G(2df), cc-pVTZ, and aug-cc-pVTZ basis sets for reasons of comparison. As shown in Table 3, the DFT results deviate significantly from the corresponding MP2 and MP4. For the geometry, our best result is  $r_{Ga-N} = 3.183$  Å (MP2/atzz) while the DFT methods give  $r_{Ga-N}$  values ranging from 2.163 to 2.793 Å, showing a reduction of up to 32%. The BSSE corrected dissociation energy with respect to  $Ga + 2N_2$  is  $D_{e2} = 2.4(2.3)$  kcal/mol and with respect to  $GaN_2 + N_2$  is  $D_{e3} = 1.4(1.3)$  kcal/mol at MP2/atzz(MP4/atzz//MP2/atzz) level of theory. The corresponding DFT values are  $D_{e2} = 0.44 - 25.8$  kcal/mol and  $D_{e3} = 0.56 - 11.6$  kcal/mol. All the above show that the DFT methodology does not predict correctly the geometry and especially the dissociation energy of the global minimum,  ${}^2m1(\tilde{X}^2B_1)$ , of the vdW  $GaN_4$  molecule compared to the MP2 and MP4 methods. It is obvious that the weakness of the DFT to predict the dispersion energy for weak vdW systems<sup>32</sup> results in yielding insufficiently accurate results. It seems that B3LYP is the most appropriate functional, but even with that, in conjunction with a large basis set of augmented triple- $\zeta$  quality, the results of the DFT calculations are not

sufficiently good; see Table 3. This is of course not unexpected, as the shortcomings of the DFT method for weakly bound systems are well known.

As far as we know, there is only one previous study for the  $GaN_4$  molecule, that of Song et al.,<sup>12</sup> who calculated three isomers using the full potential linear muffin tin orbital method, and their lowest isomer, which is the same structure as ours, has 36% shorter bond distance Ga–N than ours, showing again that such methods are not adequate for van der Waals systems.

The MP2/atzz potential energy profiles of the  ${}^2m1(\tilde{X}^2B_1)$  and  ${}^2s2({}^2\Pi_u)$  structures of the  $GaN_4$  molecule are plotted in Figure 2 as one or two  $N_2$  molecules are being removed. The optimized potential energy profile of the ground state,  ${}^2m1(\tilde{X}^2B_1)$  with respect to the angle  $\phi$  (i.e., the bending potential) at MP2/tz (upper curve) and MP2/atzz levels are shown in Figure 3. Along this profile, structure  ${}^2s2({}^2\Pi_u)$  is a transition state at the MP2/atzz level, but has no imaginary frequencies at the MP2/tz level. It should be noted that the corresponding BSSE optimized potential energy profiles at MP2/tz and MP2/atzz level have exactly the same shapes as those in Figure 3, which means that diffuse functions are necessary to determine what type of extremum  ${}^2s2({}^2\Pi_u)$  is. In the case of the  $GaN_4^+$  cation<sup>13</sup> the corresponding linear  $N\equiv N\cdots Ga^+\cdots N\equiv N$  isomer is a transition state in both MP2/tz and MP2/atzz level of theory.

Isomerization between two equivalent  $\tilde{X}^2B_1$  minima, as the wedge changes direction, occurs via the transition state, the linear  ${}^2s2$ , (Figure 1b), which has an increased  $r_{Ga-N}$  bond by  $\sim 0.1$  Å at the MP2/atzz level of theory while the barrier to isomerization is 1.1 kcal/mol; see Table 4. A contour plot of the optimized two-dimensional potential energy surface between the two  ${}^2m1(\tilde{X}^2B_1)$  minima and their transition state  ${}^2s2({}^2\Pi_u)$  at the MP2/atzz level is given in Figure 4.

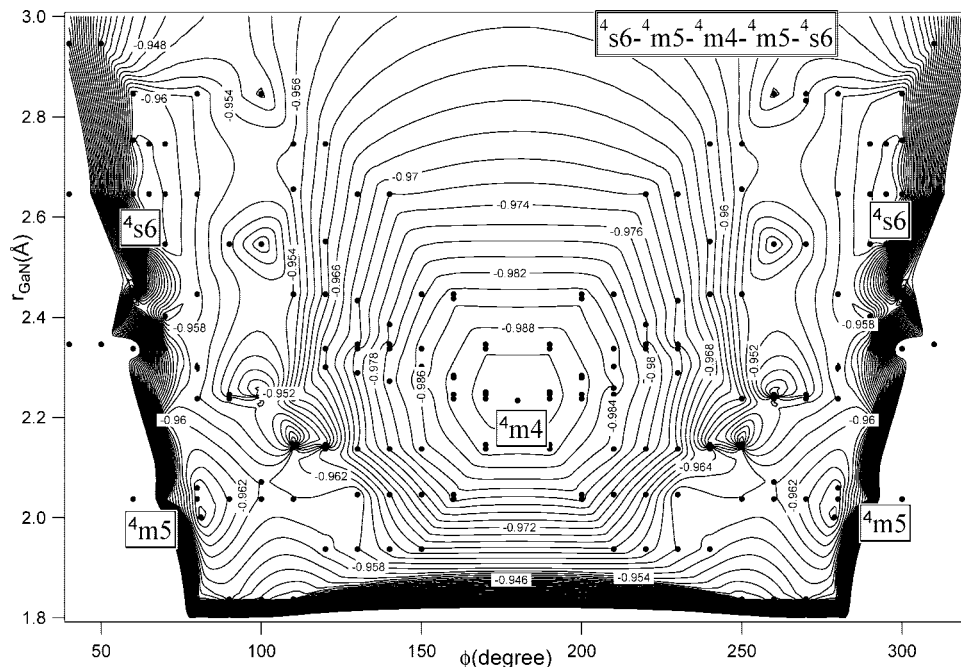
Harmonic frequencies of  ${}^2m1$  and  ${}^2s2$  at MP2/tz and MP2/atzz level of theory are given in Table 5. The frequencies  $\omega_2$  to  $\omega_7$  ( ${}^2m1$ ) and  $\omega_3$  to  $\omega_8$  ( ${}^2s2$ ) are all within a narrow range of 10  $cm^{-1}$ ; consequently the ordering of frequencies of stretching and bending modes is different in the two basis sets. Compared to the frequencies of the modes of  $GaN_2(\tilde{X}^2\Pi)$  and  $GaN_4(m1)$ , they show small shifts ranging in an interval of  $\pm 44$   $cm^{-1}$ . The one imaginary frequency of  ${}^2s2$  corresponds to the bending of the linear  $N-N-Ga-N-N$ .

The third isomer  ${}^2m3$  is a cyclic minimum (see Figure 1c) with  $r_{Ga-N} = 2.280$  Å and  $\phi_{NGa} = 75.3^\circ$  at the MP2/atzz level of theory. Natural population analysis shows that the net charge of the Ga is  $+0.69$   $le^{-1}$  while the adjacent N atoms to Ga atom are negative with a net charge of  $-0.29$   $le^{-1}$ . This structure is unbound with respect to  $Ga({}^2P) + 2N_2(X^1\Sigma_g^+)$ . However, from the geometry of the molecule, it seems that Ga ( ${}^2P$ ) interacts with a rectangular cyclic  $N_4({}^3B_2)$  and the BSSE corrected dissociation energy with respect to  $Ga({}^2P) + N_4({}^3B_2)$  (optimized local minimum of the  $N_4$  molecule) is 140.6 kcal/mol.

The  ${}^4m4$ ,  ${}^4m5$ ,  ${}^4s6$ , and  ${}^4s7$  structures consist of a Ga atom in its excited state  ${}^4P$  interacting with two  $N_2(X^1\Sigma_g^+)$  molecules; see Figure 1d–g. Of these structures, the lowest-energy one,  ${}^4m4({}^4\Sigma_g^-)$ , which is the third minimum calculated for  $GaN_4$ , is a linear structure lying 70.7 kcal/mol above the  ${}^2m1$  minimum, while the remaining three structures are bent with different values for the  $\phi_{NGa}$  angle. The BSSE corrected dissociation energy with respect to  $Ga({}^4P) + 2N_2(X^1\Sigma_g^+)$  is 17.6 kcal/mol and with respect to  $GaN_2(\tilde{a}^4\Sigma^-) + N_2(X^1\Sigma_g^+)$  is 1.9 kcal/mol for the  ${}^4m4$  isomer. The  ${}^4m5$  minimum is a cyclic minimum and it lies 14.1 kcal/mol above the linear  ${}^4m4$  isomer. It should be noted that some DFT calculations give larger  $\phi_{NGa}$  and  $\phi_{NGa-N}$  angles than the MP2 leading to an open cyclic minimum







**Figure 6.** Potential energy surface of  $4s6-4m5-4m4-4m5-4s6$  as a function of the Ga–N distance and the  $\varphi_{\text{NGaN}}$  angle represented by contour lines equally spaced by 0.002 hartree at the MP2/aug-cc-pVTZ level of theory. The contour lines were drawn based on the data calculated at the coordinates represented by the filled circles.

N atoms at the end have about  $-0.02$  each, while the N atom closer to Ga has gained  $-0.29$   $\text{e}^-$ .

The  $4m11$  isomer is a cyclic minimum with quartet spin symmetry, see Figure 1k, with  $r_{\text{Ga-N}} = 2.150$  Å and  $\varphi_{\text{NGaN}} = 71.3^\circ$  at the MP2/atz level of theory. Natural population analysis shows that the Ga atom is in its ground state,  $^2\text{P}$ , with a net charge of  $+0.71$   $\text{e}^-$  while the adjacent N atoms are negative with a net charge of  $-0.35$   $\text{e}^-$ . Thus, the  $\text{Ga}(^2\text{P})$  atom is connected to a trapezoid  $^3\text{N}_4(^3\text{B}_2)$  molecule. The BSSE corrected dissociation energy with respect to  $\text{Ga}(^2\text{P}) + \text{optimized } ^3\text{N}_4(^3\text{B}_2)$  is 41.0 kcal/mol.

The  $4s8(^4\text{B}_{1u})$  is a saddle point of  $D_{2h}$  symmetry (see Figure 1h), and the imaginary frequencies correspond to movements of  $\text{N}_2$  out of the plane of the molecule. It consists of  $\text{Ga}(^2\text{P}) + 2 \text{N}_2(^3\Pi_g)$  with a BSSE diabatic binding energy of 232 kcal/mol. The  $^2s10$  and  $4s14$  isomers are T-shaped structures consisting of either a triangular  $\text{GaN}_2$  and a  $\text{N}_2$  connected with a bond to Ga, or a linear  $\text{GaNN}$  whose Ga interacts with the  $\text{N}_2$  triple bond; see Figure 1j,n. The  $^2s10$  isomer has one frequency which corresponds to a movement in the plane of the  $\text{N}_2$  around the  $\text{C}_2$  axes and the  $4s14$  isomer has two imaginary frequencies which correspond the first one to a movement of the  $\text{N}_2$  molecules out of plane and the second one in the plane. Both isomers have an excited  $\text{Ga}(^4\text{P})$  and a triplet excited  $\text{N}_2$  whose triple bond interacts with the Ga atom. The BSSE corrected dissociation energies of the isomers with respect to  $\text{N}_2(^1\Sigma_g^+) + \text{N}_2(^3\Sigma_u^+) + \text{Ga}(^4\text{P})$  are 114( $^2s10$ ) and 98( $4s14$ ) kcal/mol, while they are unbound with respect to the ground-state products  $\text{Ga}(^2\text{P}) + 2\text{N}_2(^1\Sigma_g^+)$ .

The  $^2s9$ ,  $^2s12$ , and  $4s17$  isomers are linear structures; see Figure 1, panels i, l, and q, respectively. All structures have the Ga atom in the ground state  $^2\text{P}$ . The BSSE corrected dissociation energy with respect to  $\text{Ga}(^2\text{P}) + \text{optimized } \text{N}_4(^1\Sigma)$  is 54.8 kcal/mol for  $^2s12$  and with respect to  $\text{Ga}(^2\text{P}) + \text{optimized } \text{N}_4(^3\Sigma)$  is 1.5 kcal/mol for  $4s17$ .

The  $^2m13$  isomer consists of a cyclic  $\text{N}_4$  molecule connected to the  $\text{Ga}(^2\text{P})$  atom. The BSSE corrected dissociation energy

with respect to  $\text{Ga}(^2\text{P}) + \text{optimized cyclic } \text{N}_4(^3\text{B}_2)$  is 67.9 kcal/mol. The  $4s15$  isomer has one imaginary frequency which corresponds to a movement of  $\text{N}_4$  out of plane. It consists of  $\text{Ga}(^2\text{P})$  interacting with a triplet  $\text{N}_4$  with a BSSE corrected dissociation energy of 44.9 kcal/mol. Finally, the  $4m16$  minimum consists of  $\text{Ga}(^4\text{P})$  connected with two N atoms and one  $\text{N}_2(^1\Sigma_g^+)$ , see Figure 1p. The BSSE corrected dissociation energy with respect to  $\text{Ga}(^4\text{P}) + 2\text{N}(^4\text{S}) + \text{N}_2(^1\Sigma_g^+)$  is 153.7 kcal/mol.

## V. Conclusions and Comments

Employing perturbation theory (MP2, MP4/aug-cc-pVTZ) the gallium dinitride,  $\text{GaN}_2$  and the gallium tetranitride molecules,  $\text{GaN}_4$ , were systematically examined. Seven ( $\text{GaN}_2$ ) and thirty-seven ( $\text{GaN}_4$ ) electronic structures were determined. Their geometries, dissociation energies, and harmonic frequencies are reported, and potential energy profiles, potential energy surfaces, and the bonding mechanisms of some lowest states are given. Our findings can be summarized as follows.

1. The ground-state of  $\text{GaN}_2$  ( $\tilde{X}^2\Pi$ ) is a linear van der Waals molecule  $\text{N}\equiv\text{N}\cdots\text{Ga}$  with  $r_{\text{Ga-N}} = 3.306$  Å and dissociation energy of 1.1 kcal/mol with respect to  $\text{Ga}(^2\text{P}) + \text{N}_2(^1\Sigma_g^+)$  products.

2. The next minimum is the  $\tilde{a}^4\Sigma^-$  state ( $\text{NNGa}^+$ ,  $r_{\text{Ga-N}} = 2.002$  Å) and the reaction energy of  $\text{GaN}_2(\tilde{a}^4\Sigma^-) \rightarrow \text{Ga}(^2\text{P}) + \text{N}_2(^1\Sigma_g^+)$  is 14.5 kcal/mol.

3. The ground electronic state of  $\text{GaN}_4$  is a triangular structure of  $^2\text{B}_1(\text{C}_{2v})$  symmetry with a  $D_e$  of 2.4 and 1.4 kcal/mol with respect to  $\text{Ga}(^2\text{P}) + 2\text{N}_2(^1\Sigma_g^+)$  and to  $\text{GaN}_2(\tilde{X}^2\Pi) + \text{N}_2(^1\Sigma_g^+)$ , respectively. The energy of isomerization between two equivalent  $\tilde{X}^2\text{B}_1$  as the wedge changes direction via a linear state ( $\text{N}-\text{N}-\text{Ga}-\text{N}-\text{N}$ ) is 1.1 kcal/mol.

4. The second ( $^2\text{A}_1$ ) minimum is a cyclic structure, lying 19.6 kcal/mol above the ground state.

5. The lowest quartet minimum of  $\text{GaN}_4$  is a linear structure of  $^4\Sigma_g^-$  ( $D_{\infty h}$ ) symmetry with a  $D_e = 17.6$  and 1.9 kcal/mol

with respect to Ga(4P) + 2N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and GaN<sub>2</sub>( $\tilde{a}^4\Sigma^-$ ) + N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), respectively.

6. A DFT study of the ground-state of GaN<sub>4</sub>, employing different combinations of functionals and basis sets did not yield sufficiently accurate results, as might be expected since GaN<sub>4</sub> is a weakly bound and the dispersion energy of such systems usually is not well described by DFT. It seems that of the different combinations examined, B3LYP in conjunction with a large basis set of augmented triple- $\xi$  quality gives the best results within the DFT methodology.

**Acknowledgment.** Financial support has been provided by the Greek General Secretariat for Research and Technology through a Greece-Slovakia bilateral collaboration program. Partial support of this work through the “Excellence in the Research Institutes” program, supervised by the General Secretariat for Research and Technology/Ministry of Development, Greece (Phase I and II, Projects 64769 and 2005ΣΕ01330081), is gratefully acknowledged.

**Supporting Information Available:** The optimized geometries of all 37 structures of doublet and quartet GaN<sub>4</sub> species at DFT(B3LYP/LANL2DZ) and MP2/[6-311+G(2df), cc-pVTZ, and aug-cc-pVTZ] level of theory are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Matsubara, H.; Yoshimoto, S.; Saito, H.; Jianglin, Y.; Tanala, Y.; Noda, S. *Science* **2008**, *319*, 445.
- (2) Goldberger, J.; He, R.; Zhang, Y.; Lee, S.; Yan, H.; Choi, H.-J.; Yang, P. *Nature* **2003**, *422*, 599.
- (3) Nakamura, S. *Science* **1998**, *281*, 956.
- (4) For example, Fuchs, M.; Da Silva, J. L. F.; Stampfl, C.; Neugebauer, J.; Scheffler, M. *Phys. Rev. B* **2002**, *65*, 245212.
- (5) BelBruno, J. J. *Heteroat. Chem.* **2000**, *11*, 281.
- (6) Kandalam, A. K.; Blanco, M. A.; Pandey, R. *J. Phys. Chem. B* **2001**, *105*, 6080. 2002, 106, 1945.
- (7) Denis, P. A.; Balasubramanian, K. *Chem. Phys. Lett.* **2006**, *423*, 247.
- (8) Šimová, L.; Tzeli, D.; Urban, M.; Černušák, I.; Petsalakis, I.; Theodorakopoulos, G. *Chem. Phys.* **2008**, *349*, 98.
- (9) Kandalam, A. K.; Pandey, R.; Blanco, M. A.; Costales, A.; Recio, J. M.; Newsam, J. M. *J. Phys. Chem. B* **2000**, *104*, 4361.
- (10) Zhou, M.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 1648.
- (11) Wang, C.-S.; Balasubramanian, K. *Chem. Phys. Lett.* **2004**, *404*, 294.
- (12) Song, B.; Cao, P.-L. *Phys. Lett. A* **2004**, *328*, 364.
- (13) Tzeli, D.; Petsalakis, I.; Theodorakopoulos, G. *J. Phys. Chem. A* **2007**, *111*, 8892.
- (14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
- (15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (16) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
- (17) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (18) Perdew, J. P.; Burke, K.; Ernzerhov, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (19) (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Canadian J. Phys.* **1980**, *58*, 1200. (b) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
- (20) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.
- (21) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Wilson, A. K.; Wood, D. E.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *110*, 7667.
- (22) Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol. Phys.* **1988**, *65*, 1321.
- (23) Curtiss, L. A.; McGrath, M. P.; Blandeau, J.-P.; Davis, N. E.; Binning, R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.
- (24) Demovič, L.; Černušák, I.; Theodorakopoulos, G.; Petsalakis, I. D.; Urban, M. *Chem. Phys. Lett.* **2007**, *447*, 215.
- (25) Tzeli, D.; Tsekouras, A. A. *J. Chem. Phys.* **2008**, *128*, 144103.
- (26) (a) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. (b) Liu, B.; Mclean, A. D. *J. Chem. Phys.* **1973**, *59*, 4557. (c) Jansen, H. B.; Ros, P. *Chem. Phys. Lett.* **1969**, *3*, 140.
- (27) Tzeli, D.; Mavridis, A.; Xantheas, S. S. *J. Phys. Chem. A* **2002**, *106*, 11327.
- (28) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887.
- (29) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024.
- (30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (31) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV Constants of diatomic molecules*; Van Nostrand Reinhold Company: New York, 1979.
- (32) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; 2nd Edition: Wiley-VCH: Weinheim, 2001.

JP8019396