

Structural, Vibrational, Thermodynamic and Frontier Molecular Orbital Studies on $(\text{GaN})_2$: A DFT and MP2 Approach

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Abstract— We report the structural, vibrational, thermodynamic and frontier molecular orbital (FMO) studies on $(\text{GaN})_2$ using density functional theory (DFT) and ab initio MP2 methods, in conjunction with the 6-31G(d) and 6-311+G(d) basis sets. The investigations carried out also for various temperature and pressure values. The geometries, the Mulliken atomic charges, and HOMO-LUMO energy were calculated for the GaN and $(\text{GaN})_2$ molecules. FT-IR and Raman spectral results were analyzed. Thermodynamic parameters such as thermal energy, thermal correction to enthalpy (ΔH), thermal correction to Gibbs free energy (ΔG), constant volume molar heat capacity (C_v) and entropy (S) were calculated for various temperatures and pressures and their results were qualitatively discussed. The results obtained give new insight of the modified structure of semiconducting material GaN. The compound $(\text{GaN})_2$ was found to have high thermal stability and enhanced semiconductor properties compared with the GaN.

Index Terms— Gallium nitride, density functional theory, HOMO-LUMO, FT-IR, Raman, thermal correction to enthalpy (ΔH), thermal correction to Gibbs free energy (ΔG), constant volume molar heat capacity (C_v), entropy (S)

1 INTRODUCTION

Gallium nitride (GaN) has gained considerable attention due to its wide and direct band gap (3.39 eV at room temperature), and strong resistance to radiation. GaN based materials are expected to be a good candidate for high-power electronic devices, light-emitting diodes, and laser diodes in the blue and UV wavelength regions [1-3]. In recent years, more and more research efforts have been devoted to the one-dimensional nanoscale materials because of their fascinating electronic, optical and mechanical properties in fabrication of novel nano devices. Electronic and optoelectronic devices made of GaN and related materials have been designed such as high-temperature, high- power transistors blue and UV LEDs [4-7]. The GaN material studied here is commercially available with many applications such as short-wavelength light-emitting diodes and high power, high frequency transistors [8]. Additionally, the GaN nano wires are of interest due to the giant electro gyration effects [8, 9]. In the present study, the structure, the thermal and the electronic properties of $(\text{GaN})_2$ have been investigated at different temperatures and different pressures.

2 COMPUTATIONAL PROCEDURE

The electronic structures and the thermodynamical properties of the GaN ($^1\Sigma^+$) and of the $(\text{GaN})_2$ (1A_1) molecules were computed via geometry optimization at the B3LYP[10]/6-31G(d) [11] level of theory. In order to test our DFT data, and to test the necessity of the diffuse functions, additional calculations using the 6-311+G(d) [11] and via the ab initio second-order Møller-Plesset Perturbation Theory (MP2) method, i.e., B3LYP/6-311+G(d), MP2/6-31G(d), and MP2/6-311+G(d) were carried out. The theoretical thermodynamic quantities are derived from the enthalpy and entropy values. It has been

shown that the B3LYP calculation of the entropy for a series of diatomic and polyatomic molecules is in excellent agreement with available experimental data [12]. All calculations have been carried out with the Gaussian09 package [13].

3 RESULTS AND DISCUSSION

3.1 Geometries and Energetics

The optimized molecular structure of the GaN ($^1\Sigma^+$) and $(\text{GaN})_2$ (1A_1) molecules are shown in Fig. 1. Their geometries and the Mulliken analysis are presented in Tables 1-2.

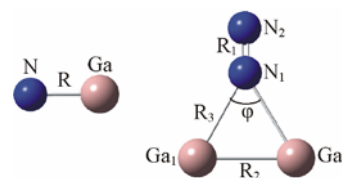


Fig. 1. Calculated geometry optimized structure of the GaN ($^1\Sigma^+$) and $(\text{GaN})_2$ (1A_1) molecules.

Form Table 1, we see that both B3LYP and MP2 methods are in general agreement and in agreement with high level ab initio methods including relativistic effects, i.e., CCSD(T)+DKH/aug-cc-pCV5Z [14]. For the GaN ($^1\Sigma^+$) molecule, we found a bond distance of about 1.73 Å via the B3LYP method, while the MP2 method predicts a shorter value of 1.70 Å. The CCSD(T)+DKH/aug-cc-pCV5Z [14] predict bond distances that range between 1.70 and 1.76 depending on the number of the correlated electrons. The best value is 1.70 Å in excellent agreement with our MP2 results. The dissociation energy, i.e., the energy that is needed to be separated the two

atoms is very high. We found to be 3.33-3.79 eV depending on the used method, while the best given value is 3.54 eV at CCSD(T)+DKH/aug-cc-pCV5Z [14]. Finally, we observe that the addition of the diffuse functions in the 6-31G(d) basis set is not necessary, and that the B3LYP method predicts data that are in agreement with high level ab initio methods. Thus, for the study of the GaN molecule the B3LYP/6-31G(d) method is a good one.

TABLE 1

Energies, E(hartree), bond length, R(Å), dissociation energy, D_e (eV), Mulliken charges on N, q_N (e⁻), dipole moments, μ (Debye) of the GaN(Σ^+) molecule at different levels of theory.

Method ^a	Energy	R	D_e	q_N	μ
B3LYP/1	-1977.49801	1.730	3.79	-0.43	4.03
B3LYP/2	-1979.45677	1.723	3.62	-0.56	4.47
MP2/1	-1975.67993	1.706	3.38	-0.40	5.47
MP2/2	-1977.68534	1.702	3.33	-0.58	5.91
CCSD(T) ^b		1.758 (1.695)	3.54		4.24 (3.94)

^a 1: 6-6-31G(d), 2: 6-311+G(d). ^b CCSD(T)+DKH/aug-cc-pCV5Z, 8(28) correlated electrons, Ref. [14].

TABLE 2

Energies, E(hartree), bond lengths, R(Å), angles, ϕ (degrees), dipole moments, μ (Debye), and Mulliken charges on N and Ga, q_N and q_{Ga} (e⁻) of the (GaN)₂ (1A_1) molecule at different levels of theory.

Method ^a	Energy	R ₁	R ₂	R ₃	ϕ
B3LYP/1	-3955.33278	1.123	2.421	2.448	59.2
B3LYP/2	-3959.23817	1.110	2.511	2.599	57.8
MP2/1	-3951.74503	1.134	2.462	2.782	52.5
MP2/2	-3955.74581	1.124	2.531	2.882	52.1
	μ	q_{N1}	q_{N2}	q_{Ga1}	q_{Ga2}
B3LYP/1	0.73	-0.04	-0.08	0.06	0.06
B3LYP/2	0.88	-0.40	0.32	0.04	0.04
MP2/1	0.43	0.01	0.01	-0.01	-0.01
MP2/2	0.19	-0.27	0.27	0.00	0.00

The (GaN)₂ (1A_1) molecule has a T-shaped structure, see Figure 2, and it is formed by the interaction of the N₂ and Ga₂ molecules. Note that while in the free N₂($X^1\Sigma_g^+$) molecule a strong triple bond is formed with a bond distance of 1.106 Å at the B3LYP/6-31G(d) level of theory; here the N₂ molecule is excited, it has a double bond, and it corresponds to the N₂($^3\Pi_g$) state with a bond distance of 1.121 Å at B3LYP/6-31G(d). The free Ga₂ ($X^3\Pi$) molecule has a bond length of 2.456 Å at B3LYP/6-31G(d). The R₁ and R₂ bond lengths are in good agreement for the four used methods. However, a large discrepancy is observed for the R₃ distance. Note, that the present B3LYP/6-31G(d) calculation predicts the shortest distance among the four method. However, MP2 calculations which carried out on neutral, cation and anion (GaN)₂ species using the aug-cc-pVTZ basis set, predict for the (GaN)₂ (1A_1) a R₃ = 2.332 Å [15]. Thus, again it seems that the B3LYP/6-31G(d) method is an adequate method for the calculation of the (GaN)₂ molecule.

3.2 Mulliken atomic charge and HOMO-LUMO orbitals

About 0.5 e⁻ is transferred from the Ga atom to the N atom in the GaN molecule via all used methods, see Table 1. In the (GaN)₂ molecule, all methods show that the Ga atoms have nearly 0 charges. However, for the N atoms, there is a discrepancy about the charges on the N atoms between the two basis sets. The addition of the diffuse functions leads to an increase of the charges of the N atoms. The N atom which forms bonds with the Ga₂ has a negative charge while the other one is positively charged.

In Fig. 2 are shown the frontiers molecular orbitals, i.e., HOMO and the LUMO orbitals. In the GaN molecule the Ga atom is excited and has a 4s¹3p² configuration. As a result, the two p electrons of the Ga atom form π bonds with the p_x and p_y electrons of the N atom. Thus, the HOMO and the HOMO-1 orbitals have the same picture, but in a different axes. In the (GaN)₂ the HOMO orbital corresponds to the bonds between Ga₂ and N₂. The HOMO-LUMO energy gap of the GaN and (GaN)₂ species has been calculated at 0.06 and 0.03 eV, respectively via the B3LYP method for both functionals. The corresponding MP2 values for both functionals are 0.36 and 0.18 eV. The HOMO-LUMO energy gap is very sensitive to the method used. However, both methods shows that the GaN molecule has a double value than the (GaN)₂ molecule.

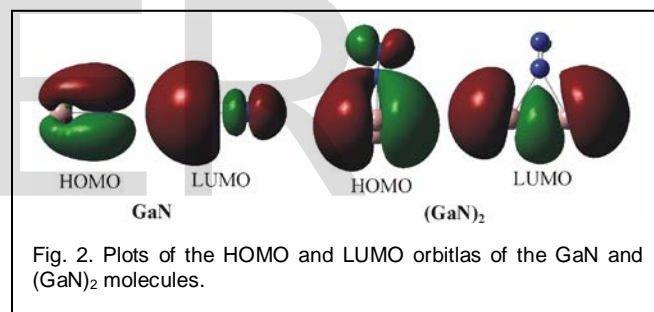


Fig. 2. Plots of the HOMO and LUMO orbitals of the GaN and (GaN)₂ molecules.

TABLE 3

Calculated frequencies (cm⁻¹), IR intensities (Km/mol) and Raman activities (Å⁴/amu) at B3LYP/6-31G(d) level of theory.

Species	Assignments	ω	IR intensity	Raman activity
GaN	ν (Ga-N)	761.8	2.0	6942
(GaN) ₂	δ (Ga-N) in plane	74.2	2.3	16.1
	ν (Ga-N)	132.4	0.9	161.4
	τ (N-N)	204.9	2.9	0.00
	ν (Ga-Ga)	205.3	0.02	485.8
	δ (N-N) out of plane	260.8	59.8	0.9
	ν (N-N)	2191.2	527.9	2277

^a ν : Stretching vibration δ : Bending vibration, τ : torsion.

3.3 FT-IR analysis

The detailed vibrational assignments of fundamental modes of (GaN)₂ and GaN were calculated. In Table 3 are given the calculated frequencies, the IR intensities and the Raman activities. For the GaN molecule, the calculated vibrational peak occurred at 761 cm⁻¹ in agreement with experimental value

[16]. For the $(\text{GaN})_2$ molecule, there are not any experimental data as far as we know. Note, that the stretching vibrations that correspond to Ga-Ga and N-N are 205 and 2191 cm^{-1} , while the corresponding values of the free $\text{Ga}_2(X^3\Pi_g)$ and $\text{N}_2(^3\Pi_g)$ are 200 and 1842 cm^{-1} at the B3LYP/6-31G(d) level of theory. Thus, while for stretching vibrations that correspond to Ga-Ga there is no difference between the free Ga_2 and $(\text{GaN})_2$, for the stretching vibrations that correspond to N-N, there is a significant blue shift of 350 cm^{-1} with respect to the free N_2 ($^3\Pi_g$). The FT-IR and Raman values of GaN and $(\text{GaN})_2$ is constant for entire calculations.

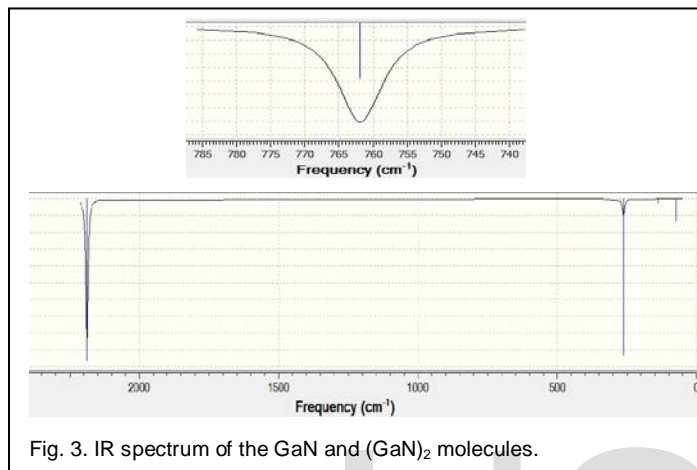


Fig. 3. IR spectrum of the GaN and $(\text{GaN})_2$ molecules.

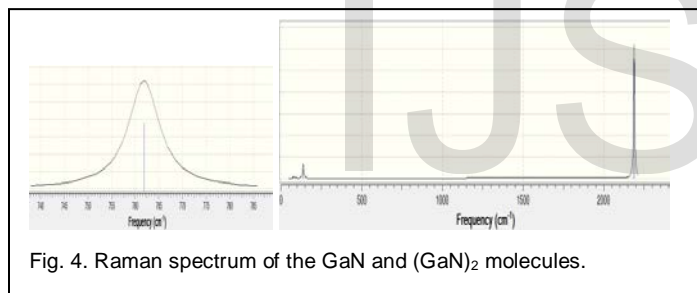


Fig. 4. Raman spectrum of the GaN and $(\text{GaN})_2$ molecules.

3.4 Analysis of thermodynamic properties

Thermal correction to enthalpy, thermal correction to Gibbs free energy, E (Thermal), C_v and Entropy are computed at various temperature (T) using the B3LYP/6-31G(d) method. These values are shown in figures 5-9.

From the following figures, we see that the value of the thermal correction to the enthalpy of the $(\text{GaN})_2$ molecule is increased more than the corresponding value of the GaN species. Generally, the positively increase of the enthalpy of formation indicates endothermic reaction. The negatively increasing ΔG values of $(\text{GaN})_2$ were largely varied from the GaN, above the room temperature due to their temperature dependent stability. All changes in internal energy of system are due to changes in thermal energy, as a result of the heat transfer. The C_v value of $(\text{GaN})_2$ and GaN are shown in figure 8.

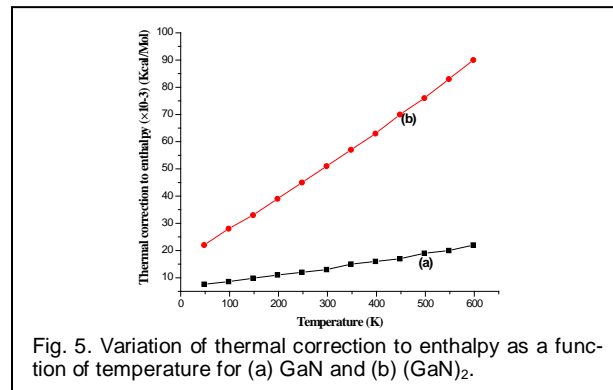


Fig. 5. Variation of thermal correction to enthalpy as a function of temperature for (a) GaN and (b) $(\text{GaN})_2$.

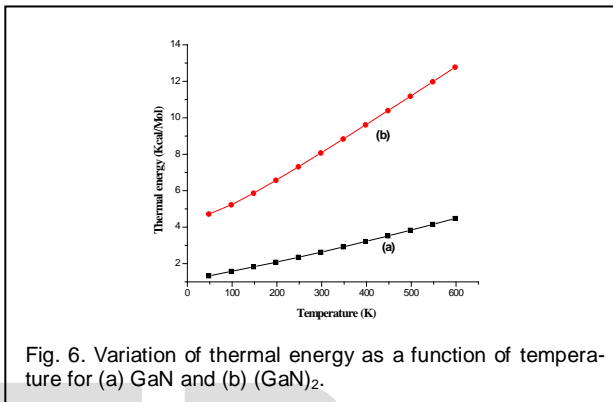


Fig. 6. Variation of thermal energy as a function of temperature for (a) GaN and (b) $(\text{GaN})_2$.

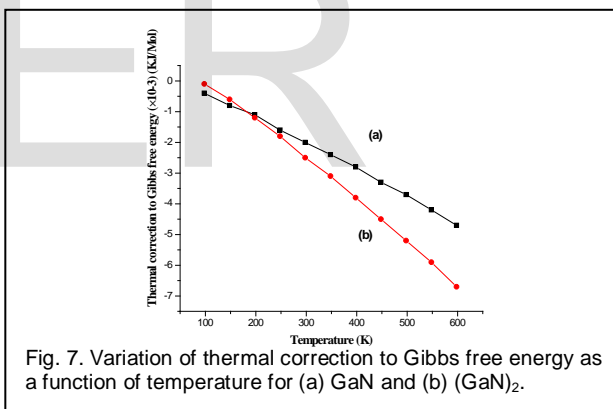


Fig. 7. Variation of thermal correction to Gibbs free energy as a function of temperature for (a) GaN and (b) $(\text{GaN})_2$.

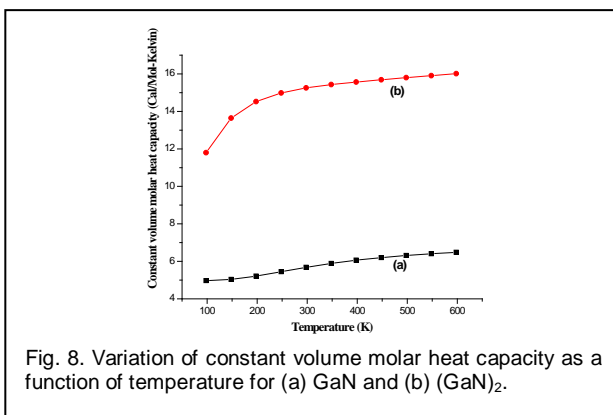


Fig. 8. Variation of constant volume molar heat capacity as a function of temperature for (a) GaN and (b) $(\text{GaN})_2$.

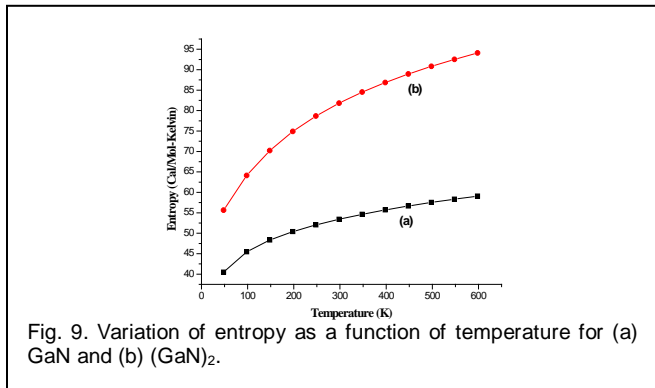


Fig. 9. Variation of entropy as a function of temperature for (a) GaN and (b) $(\text{GaN})_2$.

Thermal correction to Gibbs free energy and entropy values for GaN and $(\text{GaN})_2$ are calculated at various pressures (atm). Thermal correction to Gibbs free energy values and entropy values for GaN and $(\text{GaN})_2$ were plotted against the pressure in Figure 10-11. From the figure 10, negatively decreasing values of Gibbs free energy indicate reduced stability of the structure when the pressure is increased. Entropy values of GaN and $(\text{GaN})_2$ are decreased when the pressure values are increased, a typical behavior for the most materials. That can be attributed to the high order of the present compounds.

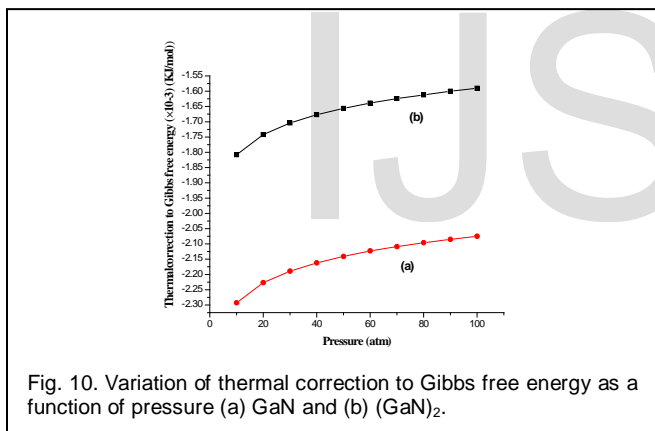


Fig. 10. Variation of thermal correction to Gibbs free energy as a function of pressure (a) GaN and (b) $(\text{GaN})_2$.

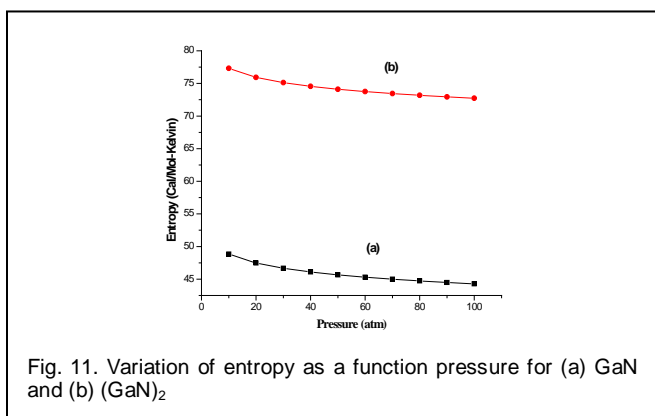


Fig. 11. Variation of entropy as a function pressure for (a) GaN and (b) $(\text{GaN})_2$

calculations. Their structure, their IR and Raman spectra, and their thermodynamic properties for various temperature and pressure values were calculated. We found that the B3LYP/6-31G(d) method is an adequate method for the calculation of the GaN and $(\text{GaN})_2$ molecule with respect to ab initio methods using large basis set. As a result, it seems that it could provide with reliable thermodynamic properties. The compound $(\text{GaN})_2$ was found to have high thermal stability and enhanced semiconductor properties compared with the GaN.

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4 SUMMARY AND CONCLUSIONS

We study the GaN and $(\text{GaN})_2$ molecules via DFT and MP2