

The low-lying electronic states of the GaN molecule

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Abstract

High-level multireference calculations are reported for the low-lying electronic states of GaN. Using the CASSCF/MRSDCI approach and the aug-cc-pVQZ basis set a detailed analysis is given for the 22 electronic states that dissociate in the first two channels. The ground state is confirmed as ($X^3\Sigma^-$) but the first excited state ($(1)^3\Pi$) is found to be very close in energy. A very accurate spectroscopic characterization is made for the lowest-lying triplet and singlet states. The behavior of dipole moment and transition dipole moment with internuclear distance is also described. Relative intensities are predicted using the Einstein coefficients.

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1. Introduction

Gallium nitride is probably the most important semiconductor material after silicon. It is a central system in large gap research for the generation of high frequency light. The electronic spectrum of gallium nitride diatomic molecule (GaN), however, is not very well known. In fact, it has been much less investigated, both theoretically and experimentally, than gallium monoxide and gallium monohalides. The isovalent AlN and GaAs species have also received more attention than the GaN molecule. All of these metal species are strong candidates for the development of new semiconductor materials, and they are very important in many areas of technological applications and fundamental science [1–4].

Experimentally, the ground state and some excited states of the gallium monohalides, gallium monoxide, AlN and GaAs have been detected and characterized

[5]. This is not the case for the gallium nitride molecule. Theoretically, gallium monohalides [6,7], GaO [8], AlN [9] and GaAs [10–12] have also received more attention than gallium nitride [13]. However, concerning the excited states, to the best of our knowledge, there is only a single study focusing on the first excited state together with the characterization of the ground state [13]. In that work, the ground state of GaN was characterized to have a $^3\Sigma^-$ symmetry and the first excited state to have a $^3\Pi$ symmetry.

In this Letter, we address to the detailed characterization of several low-lying triplet and singlet electronic states of GaN using a high-level correlation method. With the purpose of providing results that can contribute to future spectral analysis and spectroscopic characterization of this molecule, the present description includes potential energy curves, spectroscopic constants, dissociation energies, transition moment functions, and radiative transition probabilities. A comparison of the electronic structure and spectra with similar studies on the isovalent AlN [9] and GaAs [10–12] molecules is also made whenever necessary.

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2. Methods

According to the Wigner–Witmer rules [14], there are 22 electronic states of the GaN molecule which, when extended to the separated atom limit, correlate with the two lowest dissociation channels. These states are: ${}^3\Sigma^-(1)$, ${}^3\Pi(1)$, ${}^5\Sigma^-(1)$, and ${}^5\Pi(1)$ correlating with the first dissociation channel, $\text{Ga}({}^2P_u) + \text{N}({}^4S_u)$, and ${}^1\Sigma^-(2)$, ${}^1\Pi(3)$, ${}^1\Delta(2)$, ${}^1\Sigma^+(1)$, ${}^1\Phi(1)$, ${}^3\Sigma^-(2)$, ${}^3\Pi(3)$, ${}^3\Delta(2)$, ${}^3\Sigma^+(1)$ and ${}^3\Phi(1)$ correlating with the second channel, $\text{Ga}({}^2P_u) + \text{N}({}^2D_u)$. The present electronic calculations involved two steps. In the first, the aim was to assess the importance of the static electron correlation effects and to define a common set of molecular orbitals to be used for all states in each spin symmetry. In the second step, one was mainly concerned with incorporating as much dynamic electron correlation as possible in the final wavefunction having in mind a balance between its dimension and computation effort. The atomic basis functions used was the augmented correlation-consistent polarized valence quadruple-zeta (aug-cc-pVQZ) type developed by Dunning and collaborators [15,16] available at the Extensible Computational Chemistry Environment Basis Set Database [17].

The first step consisted of state-averaged complete active space self-consistent field (CASSCF) [18,19] calculations separately for each set of triplet, singlet, and quintet spin symmetries. At the C_{2v} point group, the 17 triplet states are distributed according to the symmetry representations $A_1(3)$, $B_1(5)$, $B_2(5)$, and $A_2(4)$; the 15 singlet states are distributed according to $A_1(3)$, $B_1(4)$, $B_2(4)$, and $A_2(4)$; and the three quintet states are distributed according to $B_1(1)$, $B_2(1)$, and $A_2(1)$. Within each spin symmetry, averaged natural orbitals were computed using the CASSCF wavefunctions, which contained all possible electronic excitations resulting from the distribution of eight electrons into eight active orbitals (4,2,2,0), which comprised the valence orbitals. The final multireference configuration interaction wavefunction (MRCI) was generated from all single and double excitations from the reference set formed by the all CASSCF configurations. The MRCI wavefunction was constructed by the internally contracted approach [20,21] implemented in the MOLPRO suite of programs [22]. Energies were calculated at intervals of 0.1 a_0 for distances from 2.5 until 5.0 a_0 , and 0.2 a_0 for distances from 5.0 until 7.0 a_0 .

For the range of internuclear distances investigated, cubic spline fits to the calculated points generated potential energy functions used in the solution of Schrödinger radial equation for the nuclear motion by the program INTENSITY [23], which besides calculating vibrational–rotational energies and vibrational wavefunctions, allowed also for the calculation of radiative transition probabilities and radiative lifetimes.

Transition probabilities for emission as given by the Einstein $A_{v'v''}$ coefficients have been obtained by the expression

$$A_{v'v''} = 7.2356 \times 10^{-6} |\langle v' | \mu_{\text{TM}}(R) | v'' \rangle|^2 v_{v'v''}^3 \frac{(2 - \delta_{0,A'+A''})}{(2 - \delta_{0,A'})},$$

where $\mu_{\text{TM}}(R)$ is the electronic transition moment function, $\langle v' |$ and $|v'' \rangle$ symbolize the upper and lower vibrational state wavefunctions, $v_{v'v''}$ is the transition energy, and $(2 - \delta_{0,A'+A''})/(2 - \delta_{0,A'})$ is the degeneracy factor. The numerical constant is the appropriate factor to express the probabilities in s^{-1} , when the transition moment is given in units of $\text{e}\text{\AA}$, and the energy in cm^{-1} . Radiative lifetimes were evaluated as the inverse of the total Einstein $A_{v'}$ coefficients. The dissociation energies (D_e) were estimated within the supermolecule approach with energies calculated up to $R = 20.0 a_0$ for the states $(1)^5\Pi$ and $(1)^3\Sigma^+$ for the first and second dissociation channels, respectively. The other spectroscopic constants were evaluated by standard fitting procedures [14].

3. Results and discussion

The calculated 22 lowest-lying electronic states of the GaN, correlating with the first and second dissociation channels, are shown in Figs. 1 and 2 for different multiplicities. Table 1 summarizes the spectroscopic constants calculated for the triplet and singlet states along with previous theoretical results. Table 2 lists the important electronic configurations as obtained from the MRCI wavefunctions around the equilibrium distances. In Figs. 3 and 4 are presented the dipole moment functions for the selected triplet and singlet states. The transition moment functions for some selected transitions are displayed in Fig. 5. The ordering of the lowest states is that of the isovalent AlN and GaAs species [9–12].

To assess the reliability of the present calculations, we first note that the energy separation in the asymptotic limits is equal to 2.44 eV, calculated as the energy difference between the states $(1)^5\Pi$ and $(1)^3\Sigma^+$ at $R = 20.0 a_0$. This result can be directly compared with the experimental atomic terms separation between the states 4S_u and 2D_u of nitrogen, which is equal to 2.38 eV [24]. This very good agreement, with a difference of 0.06 eV, is similar to recent results calculated for PCI molecule [25].

Our calculations indicate that the ground state of GaN has symmetry $X^3\Sigma^- (\dots 10\sigma^2 11\sigma^2 4\pi^2)$ and the first excited state has symmetry ${}^3\Pi (\dots 10\sigma^2 11\sigma^1 4\pi^3)$. This is in agreement with previous fourth-order multireference coupled pair approximation (MRCPA-4) [13]. These two electronic states correlate with the first dissociation channel, $\text{Ga}({}^2P_u) + \text{N}({}^4S_u)$, and are separated by only 0.08 eV. As calculations carried out with state-averaged

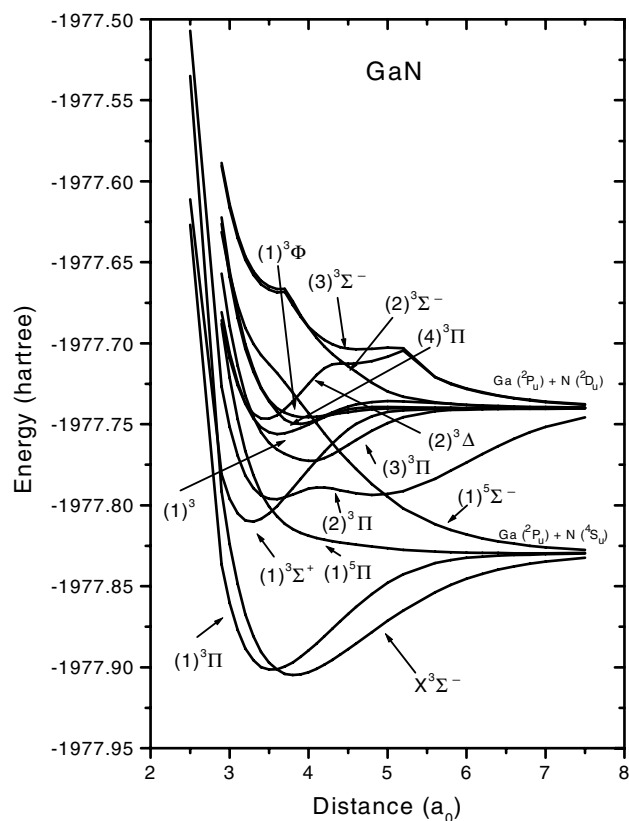


Fig. 1. Potential energy curves for the low-lying triplet and quintet electronic states of GaN.

natural orbitals may lead to a slightly less accurate description of the ground state, we found convenient to carry another set of calculations for each state ($X^3\Sigma^-$ and $(1)^3\Pi$); first using CASSCF (8,8) and second using MRCI wavefunctions. The corresponding MRCI T_e value is equal to 0.07 eV, in agreement with the previous result. As a comparison, the value calculated with MRCPA-4 correlating only the valence electrons is equal to 0.29 eV [13]. The $(1)^3\Pi$ state has shorter equilibrium distance ($R_e = 3.54 a_0$) than the ground state, $X^3\Sigma^-$ ($R_e = 3.82 a_0$). The MRCPA-4 R_e values are, respectively, equal to 3.64 and $3.82 a_0$ [13]. The dissociation energies (D_e) for the $X^3\Sigma^-$ and $(1)^3\Pi$ are, respectively, equal to 2.08 and 1.99 eV. For the $X^3\Sigma^-$, the MRCPA-4 D_e value is 1.86 eV [13]. The first two electronic states ($X^3\Sigma^-$ and $(1)^3\Pi$) are the same as for the isoivalent GaAs molecule [10–12]. However, for AlN the two lowest states are reversed, with the ground state predicted to be $^3\Pi$ and the first excited state to be $^3\Sigma^-$, but these states are separated by only 0.01 eV [9].

The two quintet states ($^5\Pi$ and $^5\Sigma^-$) also correlate with the first dissociation channel, $\text{Ga}(^2P_u) + \text{N}(^4S_u)$, but they are both repulsive (Fig. 1). At short distance, the $(1)^5\Sigma^-$ state exhibit an avoided crossing with another excited state, which was better described calculating again the quintet states with a CASSCF and MRCI

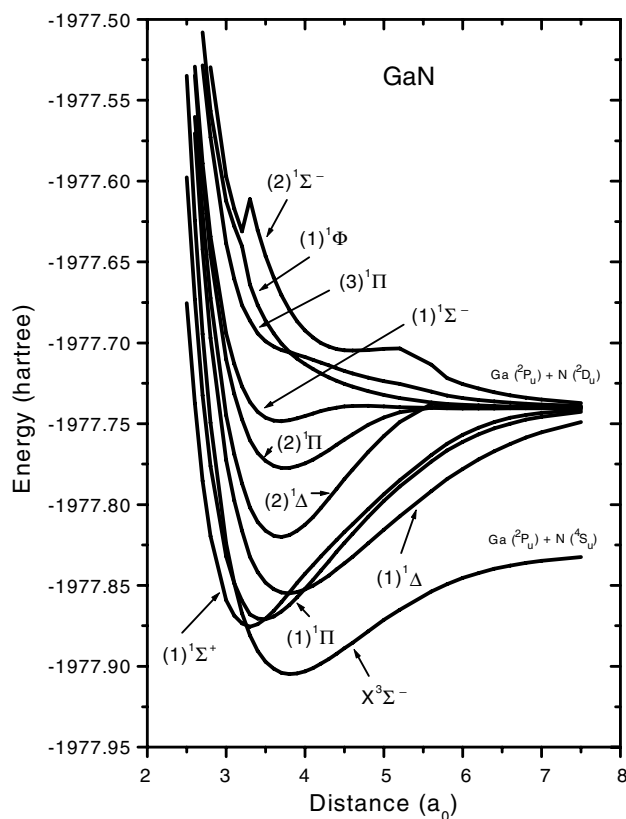


Fig. 2. Potential energy curves for the low-lying singlet electronic states of GaN.

Table 1
Spectroscopic constants of the low-lying states of GaN

	T_e (eV)	R_e (a_0)	D_e (eV)	ω_e (cm^{-1})
$X^3\Sigma^-$	0.0	3.82	2.08	502
		3.82 ^a	1.86 ^a	505 ^a
$(1)^3\Pi$	0.08	3.54	1.99	622
	0.29 ^a	3.64 ^a		583 ^a
$(1)^1\Sigma^+$	0.80	3.31	3.72	780
$(1)^1\Pi$	0.91	3.46	3.61	735
$(1)^1\Delta$	1.36	3.77	3.16	514
$(2)^1\Sigma^+$	2.30	3.68		641
$(1)^3\Sigma^+$	2.58	3.28	1.95	744
$(2)^3\Pi$	2.95	3.56		552
$(2)^1\Pi$	3.46	3.73	1.06	499
$(3)^3\Pi$	3.60	4.02	0.92	447
$(1)^3\Delta$	4.04	3.60	0.48	546
$(4)^3\Pi$	4.21	3.87	0.31	547
$(1)^1\Sigma^-$	4.25	3.67	0.27	442
$(2)^1\Delta$	4.29	3.67		450
$(2)^3\Delta$	4.30	3.45		740
$(1)^3\Phi$	4.32	4.00	0.20	374

^a Theoretical, [13].

wavefunctions involving five states, distributed according to the symmetry representations $B_1(1)$, $B_2(1)$, and $A_2(3)$ of the C_{2v} point group.

As shown in Figs. 1 and 2, the other 18 electronic states calculated here dissociate in the second channel,

Table 2
Important electronic configurations of the low-lying states of GaN

State	Dominant configuration ^a
$X^3\Sigma^-$	$\dots 10\sigma^2 11\sigma^2 4\pi^2$ (0.93)
$(1)^3\Pi$	$\dots 10\sigma^2 11\sigma^1 4\pi^3$ (0.87); $\dots 10\sigma^1 11^2 4\pi^3$ (0.27)
$(1)^1\Sigma^+$	$\dots 10\sigma^2 4\pi^4$ (0.80); $\dots 10\sigma^1 11\sigma^1 4\pi^4$ (0.24); $\dots 10\sigma^2 4\pi^3 5\pi^1$ (0.21)
$(1)^1\Pi$	$\dots 10\sigma^2 11\sigma^1 4\pi^3$ (0.89); $\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$ (0.17); $\dots 10\sigma^1 11\sigma^2 4\pi^2 5\pi^1$ (0.16)
$(1)^1\Delta$	$\dots 10\sigma^2 11\sigma^2 4\pi^2$ (0.94)
$(2)^1\Sigma^+$	$\dots 10\sigma^2 11^2 4\pi^2$ (0.60); $\dots 10\sigma^2 4\pi^4$ (0.23)
$(1)^3\Sigma^+$	$\dots 10\sigma^1 11\sigma^1 4\pi^4$ (0.71); $\dots 10\sigma^2 4^3 5\pi^1$ (0.33)
$(2)^3\Pi$	$\dots 10\sigma^1 11\sigma^2 4\pi^3$ (0.68); $\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$ (0.38)
$(2)^1\Pi$	$\dots 10\sigma^1 11\sigma^2 4\pi^3$ (0.55); $\dots 10\sigma^2 11\sigma^1 4^2 5\pi^1$ (0.47); $\dots 10\sigma^1 11\sigma^2 4\pi^2 5\pi^1$ (0.26)
$(3)^3\Pi$	$\dots 10\sigma^2 11\sigma^1 4^2 5\pi^1$ (0.50); $\dots 10\sigma^1 11\sigma^2 4\pi^3$ (0.27)
$(1)^3\Delta$	$\dots 10\sigma^2 4^3 5\pi^1$ (0.61); $\dots 11\sigma^2 4\pi^3 5\pi^1$ (0.17); $\dots 10\sigma^1 11\sigma^1 4\pi^3 5\pi^1$ (0.16)
$(4)^3\Pi$	$\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$ (0.57); $\dots 10^1 11\sigma^2 4\pi^3$ (0.35)
$(1)^1\Sigma^-$	$\dots 10\sigma^2 4\pi^3 5\pi^1$ (0.61); $\dots 11\sigma^2 4\pi^3 5\pi^1$ (0.17); $\dots 10\sigma^1 11\sigma^1 4\pi^3 5\pi^1$ (0.16)
$(2)^1\Delta$	$\dots 10\sigma^2 4\pi^3 5\pi^1$ (0.60); $\dots 11\sigma^2 4\pi^3 5\pi^1$ (0.18); $\dots 10\sigma^1 11\sigma^1 4\pi^3 5\pi^1$ (0.17)
$(2)^3\Delta$	$\dots 10\sigma^1 4\pi^3 5\pi^1$ (0.52); $\dots 10\sigma^1 11^4 4\pi^4$ (0.47)
$(1)^3\Phi$	$\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$ (0.56); $\dots 10\sigma^1 11\sigma^2 4\pi^2 5\pi^1$ (0.12)

^a Values in parentheses are the coefficients squared of the CSF associated with the electronic configuration.

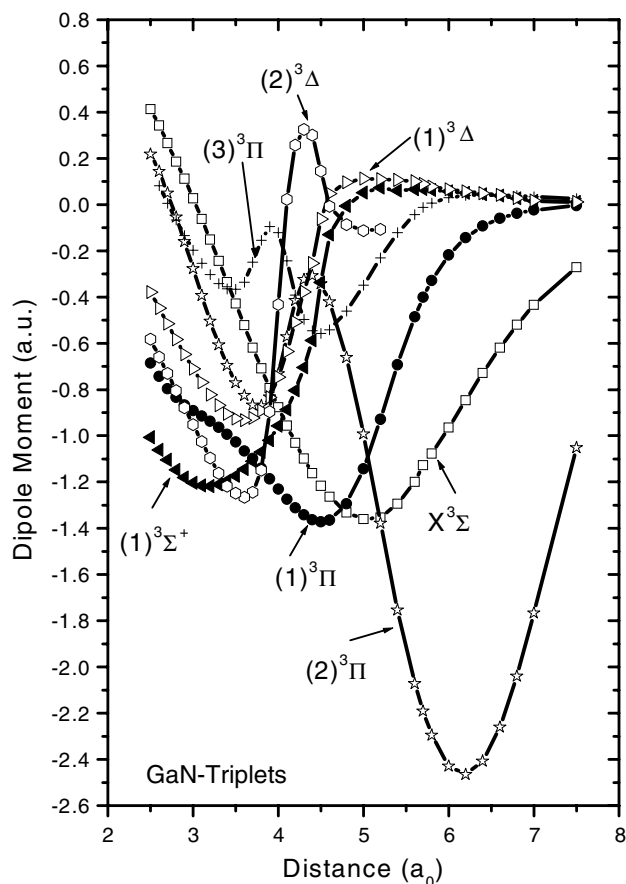


Fig. 3. Dipole moment functions for selected triplet electronic states of GaN.

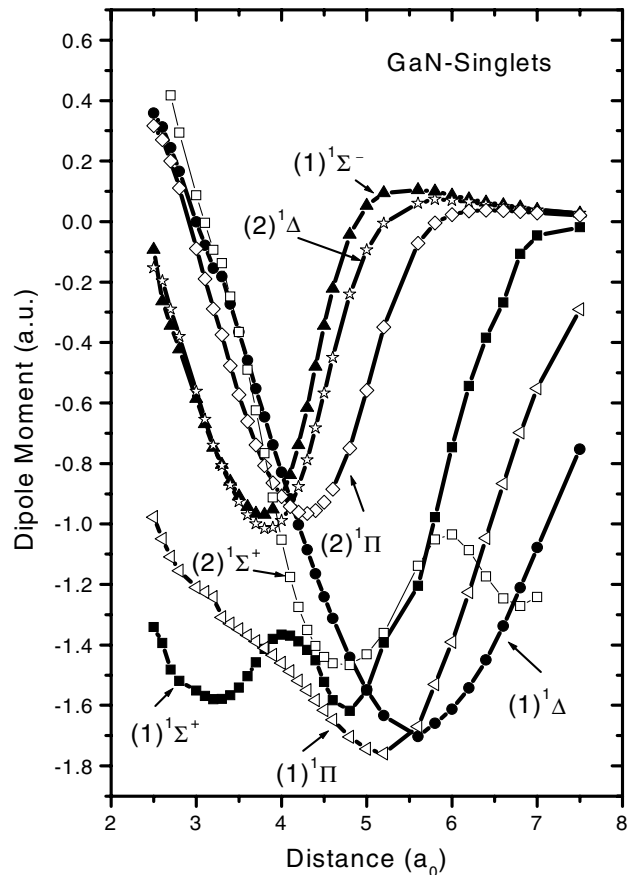


Fig. 4. Dipole moment functions for selected singlet electronic states of GaN.

$\text{Ga}(^2P_u) + \text{N}(^2D_u)$. Following the ground state, $X^3\Sigma^-$, and the first excited state, $(1)^3\Pi$, the next four excited singlet states have symmetry, $(1)^1\Sigma^+$ ($\dots 10\sigma^2 4\pi^4$), $(1)^1\Pi$ ($\dots 10\sigma^2 11\sigma^1 4\pi^3$), $(1)^1\Delta$ ($\dots 10\sigma^2 11\sigma^2 4\pi^2$) and $(2)^1\Sigma^+$ ($\dots 10\sigma^2 11\sigma^2 4\pi^2$), and are above the ground state

by 0.80, 0.91, 1.36 and 2.30 eV, respectively. The equilibrium distances for these four excited singlet states, are, respectively, 3.31, 3.46, 3.77 and 3.68 a_0 , being all smaller than the equilibrium distance of the ground state. The $(2)^1\Sigma^+$ state was not predicted initially, because it

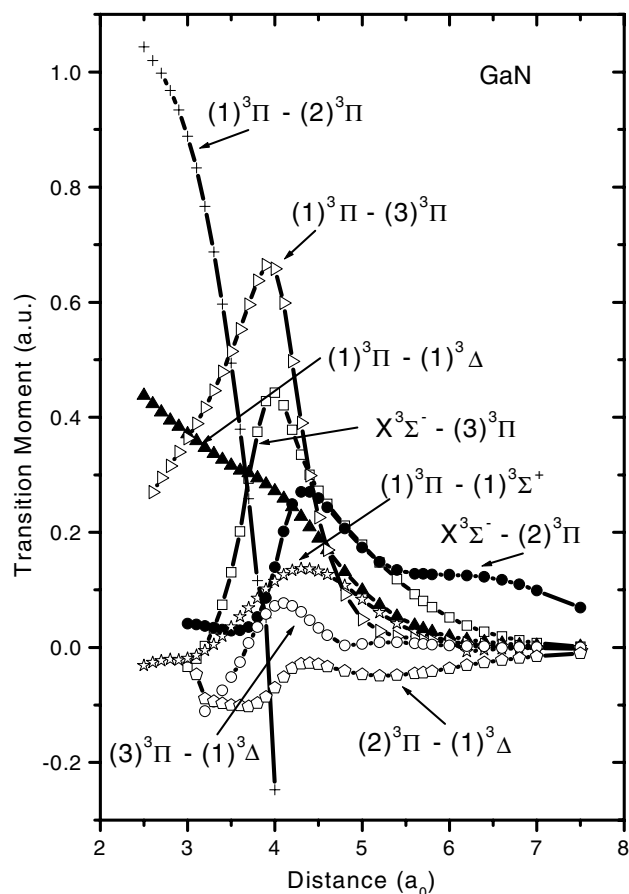


Fig. 5. Transition dipole moment functions for selected electronic transitions of GaN.

correlates with the higher third dissociation channel. Using the C_{2v} point group, at short distance it is the third state of symmetry A_1 , although at large distance the third A_1 state is $(2)^1\Delta$. In order to better describe this state, a new set of calculations for the singlet states were carried out involving 16 states distributed according to $A_1(4)$, $B_1(4)$, $B_2(4)$, and $A_2(4)$. The next excited state has triplet symmetry, $(1)^3\Sigma^+$ ($\dots 10\sigma^{11}\sigma^1 4\pi^4$) and lies 2.58 eV above the ground state. This state presents a stronger multiconfiguration character compared to the first two triplet states, and has the shortest equilibrium distance ($R_e = 3.28 a_0$) of all calculated states.

Next in energy, our study finds the states $(2)^3\Pi$ and $(2)^1\Pi$ ($\dots 10\sigma^{11}\sigma^2 4\pi^3$) with T_e respectively equal to 2.95 and 3.46 eV, and R_e equal to 3.56 and 3.73 a_0 . The state $(2)^3\Pi$ presents a avoided crossing around 4.3 a_0 with the other state of same symmetry, $(3)^3\Pi$ ($\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$), so its bound region spans a very small internuclear interval supporting only two vibrational levels. The $(3)^3\Pi$ state, in turn, presents the largest equilibrium distance, 4.02 a_0 , and is above the ground state by 3.60 eV.

The next six bound states of this study are: $(1)^3\Delta$ ($\dots 10\sigma^2 4\pi^3 5\pi^1$), $(4)^3\Pi$ ($\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$), $(1)^1\Sigma^-$

($\dots 10\sigma^2 4\pi^3 5\pi^1$), $(2)^1\Delta$ ($\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$), $(2)^1\Delta$ ($\dots 10\sigma^1 4\pi^3 5\pi^1$), and $(1)^3\Phi$ ($\dots 10\sigma^2 11\sigma^1 4\pi^2 5\pi^1$). These states present a strong multiconfigurational character, and are located at 4.04, 4.21, 4.25, 4.29, 4.30 and 4.32 eV above the ground state, respectively.

Now we analyze the results of the dipole moment functions for some selected electronic triplet and singlet states. These are presented in Figs. 3 and 4. Negative values correspond to the polarity Ga^+N^- . For all states, as expected, the dipole moments go to zero for large internuclear distances reflecting the dissociation into neutral species. For the states that present avoided crossing with a higher-lying state, the dipole moment changes abruptly in the same regions where the potential energy curves change. No experimental or theoretical data were found for comparison.

Complementing this spectroscopic description, we show in Fig. 5 the transition moment functions for some selected band systems. Using these functions, transition probabilities expressed as the Einstein coefficients and radiative lifetimes were evaluated, and are presented in Tables 3 and 4, respectively. First, note that at large distance, as expected, the transition moments go to zero reflecting a spin forbidden transition $\text{N}(^4S_u)$ to $\text{N}(^2D_u)$, since all the transitions involve states that dissociate in the two lowest dissociation channels, $\text{Ga}(^2P_u) + \text{N}(^4S_u)$ and $\text{Ga}(^2P_u) + \text{N}(^2D_u)$. As discussed before, the ground state $X^3\Sigma^-$ and the first excited state $(1)^3\Pi$ are very close in energy and therefore the transitions studied involve the emission from the excited states to these first two states. The transitions from the state $(2)^3\Pi$ to $X^3\Sigma^-$ and to $(1)^3\Pi$ involve the emission of a single electron $4\pi \rightarrow 10\sigma$ and $11\sigma \rightarrow 10\sigma$, or π bonding ($\text{N } 2p\pi + \text{Ga } 4p\pi$) \rightarrow $\text{Ga } 4s$ and σ bonding ($\text{N } 2p\sigma + \text{Ga } 4p\sigma$) \rightarrow $\text{Ga } 4s$, respectively. The transitions from the state $(3)^3\Delta$ to the states $X^3\Sigma^-$ and $(1)^3\Pi$ are more strong, since both contributions of the transition moment and the energy factor are larger than the same transitions from the state $(2)^3\Pi$. These band systems involve a single electron

Table 3

Total Einstein $A_{v'}$ coefficients (s^{-1}) for spontaneous emission of some selected triplet band systems of GaN

Transition	v'	$A_{v'}$	Transition	v'	$A_{v'}$
$(2)^3\Pi - X^3\Sigma^-$	0	21353	$(2)^3\Pi - (1)^3\Pi$	0	4285029
	1	24421		1	3796685
$(3)^3\Pi - X^3\Sigma^-$	0	8577954	$(3)^3\Pi - (1)^3\Pi$	0	13743713
	1	7469564		1	12859710
	2	6453470		2	11896505
$(1)^3\Delta - (1)^3\Pi$	0	14983915	$(1)^3\Delta - (2)^3\Pi$	0	14086
	1	14501225		1	13445
	2	13948613			
$(1)^3\Delta - (3)^3\Pi$	0	112	$(1)^3\Sigma^+ - (1)^3\Pi$	0	3814
	1	84		1	14550
	2	57		2	29652

Table 4
Radiative lifetimes (ns) for spontaneous emission of some selected triplet states of GaN

State	v'	$\tau_{v'}$
(1) ³ Σ ⁺	0	262 192
	1	68 729
	2	33 725
(2) ³ Π	0	232
	1	262
(3) ³ Π	0	44.8
	1	49.2
	2	54.5
(1) ³ Δ	0	66.7
	1	68.9
	2	71.7

transition $5\pi \rightarrow 11\sigma$ and $5\pi \rightarrow 4\pi$ or 5π antibonding (N $2p\pi - \text{Ga } 4p$) to σ bonding (N $2p\sigma + \text{Ga } 4p\sigma$) and π bonding (N $2p\pi + \text{Ga } 4p\pi$), respectively. We have also studied the band systems, $(1)^3\Sigma^+ - (1)^3\Pi$ and $(1)^3\Delta - (1)^3\Pi$. The transitions from the $(1)^3\Sigma^+$ are very weak, since the transition moment and energy factor are smaller than others transitions, and consequently the lifetimes are very long. The transitions from the $(1)^3\Delta$ and the one from the $(3)^3\Pi$ are the strongest and the radiative lifetimes from $v' = 0$ are predicted to be 66.7 and 44.8 ns, respectively.

4. Conclusions

This Letter reports high-level multireference calculations of the potential energy curves of a manifold of electronic states of GaN correlating with the first two dissociation channels. A detailed theoretical description of the ground ($X^3\Sigma^-$) and the first excited state ($(1)^3\Pi$) is presented. In addition, this study also provides a very accurate spectroscopic characterization of the lowest-lying triplet and singlet states. Dipole moment functions, transition moment functions, transition probabilities, and radiative lifetimes are reported. It is expected that the spectroscopic results reported in this work can be used by experimentalists as a reliable guide in the spectral analysis of the GaN molecule.

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