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Theoretical spectroscopic constants of the GaN molecule

Yuji Mochizuki[1], **Kiyoshi Tanaka**[2,*]

[1] Research Fellow of Japan Science and Technology Corporation, CCSE, Japan Atomic Energy Research Institute,
Nakameguro 2-2-54, Meguroku 153-0061, Tokyo, Japan
[2] Division of Natural Sciences, The University of Electro-Communications,
Chofugaoka 1-5-1, Chofu, Tokyo 182-8585, Japan

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Abstract. Fourth-order multi-reference coupled pair approximation (MRCPA-4) calculations were performed to predict spectroscopic constants of the gallium nitride (GaN) diatomic molecule. The calculations showed that the ground state is $^3\Sigma^-$ but that the $^3\Pi$ state is low lying and separated from the former by 0.5 eV. The contribution of the correlations among the Ga 3*d* semi-core electrons was found to be crucial for a quantitative description of the molecule.

Key words: Gallium nitride – Semi-core electrons –
Near degeneracy – Size consistency –
Multi-reference coupled pair approximation

1 Introduction

In our previous studies [1, 2], spectroscopic constants of the gallium hydride (GaH) and gallium fluoride (GaF) molecules, and their positive ions, were calculated by the fourth-order coupled pair approximation (CPA-4) and its MR variant (MRCPA-4) [3–7] with flexible basis sets. It was shown that the electron correlations of the Ga 3*d* semi-core shell have a sizable contribution in evaluating spectroscopic constants, with a quantitative agreement with experiment. Inclusion of not only the valence/3*d* intershell but also the 3*d* intrashell correlations was found to be necessary for the balanced and thus reliable description, although it was computationally costly. The formation of chemical bonds by the valence 4*s* and 4*p* electrons on Ga could induce differential effects on the 3*d* electrons relative to the purely atomic environment.

In a series of investigations, we predict spectroscopic constants of the gallium nitride (GaN) molecule, using the similar scheme of calculations as with our previous papers [1, 2]. No experimental or theoretical information, including the assignment of the ground state, was available for this molecule to date, although its existence has been predicted. GaN solids, which are semi-conductors, are well known to be promising emitter material for blue-region light (e.g. see [8]). Thus, experimental investigation for the growth processes, stable surface phases, and electronic properties have been extensively carried out for the solid state. Correspondingly, density-functional theory (DFT) calculations have been reported. Some of such DFT calculations took special care in treating the Ga 3*d* shell, using the so-called non-linear core correction (NLCC) in conjunction with the pseudo-potential technique [9–11]. The NLCC could incorporate the exchange and correlation contributions from the 3*d* electrons in an effective fashion. If the NLCC is not considered, the reliability of the numerical evaluation is not acceptable for a quantitative discussion of GaN solids [11]. From the viewpoint of the orbital energy, the levels of Ga 3*d* and N 2*s* are close to each other, where the values are −1.15 au for the former and −0.93 au for the latter according to the atomic self-consistent-field (SCF) procedure [12]. When the bonds form between Ga and N atoms, interactions between the N 2*s* and Ga 3*d* orbitals cannot be negligible because of such an energetic closeness. A balanced treatment for 3*d* and 2*s* would be required for a quantitative description of the Ga-N bonding.

Now, the fundamental issue to be solved is the determination of the ground state of the diatomic GaN molecule. By analogy with the isovalent molecules BN, AlN, AlP, and GaAs [13–21], there are two possible candidates: $^3\Sigma^-$ and $^3\Pi$. The former state has a single σ bond and the latter has a π bond. The energetic separation between the $^3\Sigma^-$ and $^3\Pi$ states of these species is known to be small. For example, Langhoff et al. [19] calculated that the ground state of AlN is $^3\Pi$, using the complete-active-space self-consistent-field (CASSCF) [22] and multi-reference configuration interaction (MRCI)

Present address:
*Division of Chemistry,
Graduate School of Science, Hokkaido University,
Kita 10 Nishi 8, Kita-ku 060-0810, Sapporo, Japan
Correspondence to: Y. Mochizuki
e-mail: mochi@koma.jaeri.go.jp

methods. Their assignment has been in accord with experimental observation and later calculations [20, 21]. Langhoff et al. showed that the adiabatic excitation energy (T_e) for the $^3\Sigma^-$ first excited state of AlN is less than 0.1 eV, where its energetic separation depends on the level of theory. The ground state of GaAs has been settled as $^3\Sigma^-$. The calculated separation from $^3\Pi$ was as small as ~0.2 eV for GaAs by MRCI investigations [14–17]. For both AlN and GaAs molecules, a much shorter bond length (R_e) for $^3\Pi$ was evaluated than for that of $^3\Sigma^-$. The situation in GaN may be the same. Furthermore, the introduction of Ga $3d$ correlations can provide for the contraction of R_e, as was demonstrated for the neutral state of GaH and GaF [1, 2]. Thus, for the GaN molecule, we would have a special interest in the relation between the $^3\Sigma^-$-$^3\Pi$ separation and the R_e value.

The remainder of the present paper is configured as follows. In Sect. 2, a qualitative bonding picture is given for the $^3\Sigma^-$ and $^3\Pi$ states, based on the results of preliminary calculations. Near degeneracies exist among the bonding and anti-bonding orbitals, and this requires MRCPA-4 treatment for both states. Details of the MRCPA-4 calculations are described in Sect. 3. Section 4 presents the spectroscopic constants for each state.

2 Qualitative bonding picture

The atomic ground state of the Ga atom is ^2P by the valence configuration of $4s^24p^1$ on the $3d$ semi-core shell. The N atom has the ^4S ground state by the $2s^22p^3$ configuration, where $2s$ is referred to as a valence shell. The following discussions are derived from preliminary calculations; the basis sets used for Ga and N are the same as the main calculations (refer to the first paragraph in Sect. 3).

When Ga and N atoms make a σ bond with p-type atomic orbitals (AOs), this leads to the $^3\Sigma^-$ state. Preliminary calculations indicated that this state seems to be the ground state. The main (or an SCF-type) configuration of $^3\Sigma^-$ is symbolically described as $\sigma_\mathrm{b}^2\pi_{\mathrm{b}(x)}^1\pi_{\mathrm{b}(y)}^1$. The subscript "b" for these molecular orbitals (MOs) means the "bonding" (or in-phase) combination between Ga $4p$ and N $2p$ AOs. Owing to the electronegativity of N, the component of the σ_b MO is characterized as $\lambda 4p + 2p$, where λ is a small mixing parameter. Two electrons in $\pi_{\mathrm{b}(x,y)}$ orbitals are attributed essentially to N $2p$ electrons but contribute to the total stabilization since delocalization toward the Ga $4p$ side takes place. These contributions in the $^3\Sigma^-$ state may be considered as two additional "one-electron bonds" of the π type.

The $^3\Pi$ state has a regular "two-electron bond" of the π type, where the orbital is denoted again as π_b and has a similar component character to σ_b. In the C_{2v} subset of the full $C_{\infty v}$ symmetry, the main configuration may be written as $\sigma_\mathrm{b}^1\pi_{\mathrm{b}(x)}^2\pi_{\mathrm{b}(y)}^1$. The state has additionally two "one-electron bonds" of σ and π types. For the isovalent AlN molecule, Langhoff et al. [19] pointed out that multi-reference character is prominent, especially in the $^3\Pi$ state. The present GaN molecule has similar features to AlN. By CASSCF calculations of a $4s4p/2p$ (six electrons in seven orbitals) type, the $\pi_{\mathrm{b}(x)}^2 \rightarrow \pi_{\mathrm{ab}(x)}^2$ excitation among bonding and anti-bonding MOs is observed to be responsible for the principal part of the near degeneracies in the $^3\Pi$ state, where the latter MO has the counter-mixing character of $4p$-$\lambda'2p$. The occupation numbers of active space natural orbitals (NOs) are calculated to be 1.8 for $\pi_{\mathrm{b}(x)}$ and 0.2 for $\pi_{\mathrm{ab}(x)}$, even around R_e, for the $^3\Pi$ state. In contrast, values for the $^3\Sigma^-$ state are roughly 1.97 for σ_b and 0.03 for σ_ab. The near degeneracy of $\sigma_\mathrm{b}^2 \rightarrow \sigma_\mathrm{ab}^2$ certainly exists in $^3\Sigma^-$, but its degree is less than $^3\Pi$, although a proper MR treatment is needed for both states. Through these CASSCF calculations, the much shorter R_e is obtained for the $^3\Pi$ state.

3 Details of MR calculations

The Gaussian basis set used for the Ga atom was the same as in the previous calculations [1, 2]. Thus, the Ga contracted set was $(15s12p7d4f2g)/[9s7p5d3f1g]$, where the fundamental part of this set is due to Shäfer et al. [23]. Preparation of augmentation functions was described in [1]. The N basis set was $[7s4p3d2f]$, derived similarly from then F case [2]. The basic $[6s3p]$ part was due to Shäfer et al. [23]. the polarization and/or correlating functions of $[3d2f]$ were taken from "aug-cc-pVTZ" by Dunning et al. [24, 25]. Exponents of the augmented diffuse s and p functions were 0.0598 and 0.0477, respectively. Basis set data, except for the authors' augmentation, were obtained from the internet database server at the US Pacific Northwest National Laboratory [26]. Cartesian contaminants of d, f, and g functions were deleted, and the total number of basis functions was 133.

The CASSCF procedure, in which a rather minimal active space was defined according to the results of preliminary calculations, was used to prepare the input MO set for MRCPA-4. The CAS problem was that six electrons are distributed among five orbitals for both the $^3\Sigma^-$ and $^3\Pi$ states. The C_{2v} symmetry instead of $C_{\infty v}$ was actually used, as was addressed in Sect. 2. The active orbital space for $^3\Sigma^-$, which was represented as $^3A_2$ in C_{2v}, was composed of three a_1, one b_1, and one b_2 orbitals. Three a_1 active MOs consisted essentially of Ga $4s$, $4p\sigma$, and N $2p\sigma$ AOs, and thus the near degeneracy between σ_b and σ_ab could be described with a flexibility of hybridization between Ga $4s$ and $4p$. The $4s$-dominated MO is denoted as σ_{4s}. The b_1 and b_2 active MOs corresponded to $\pi_{\mathrm{b}(x,y)}$ dominated by N $2p\pi$. For the $^3\Pi$ or $^3B_2$ state, the $4p\sigma$ (a_1) orbital of $^3\Sigma^-$ was replaced by $4p\pi_{(x)}$ (b_1) for description of the crucial $\pi_{\mathrm{b}(x)}^2 \rightarrow \pi_{\mathrm{ab}(x)}^2$ double excitation. The total numbers of configurations in CAS-CI for $^3\Sigma^-$ and $^3\Pi$ were six and eight, respectively. The numbers in configuration state functions (CSFs) were 12 for both states.

The mixing between Ga $3d\sigma$ and N $2s$ orbitals was actually found, especially for the $^3\Pi$ state having the closer Ga-N distance than $^3\Sigma^-$. The orbital energy of a "$3d\sigma$" type MO is lowered and that of a "$2s$" is raised by the mixing. In previous studies for GaH [1] and GaF [2], the following correlating schemes were used:

1. V: only valence electrons are correlated.
2. CV: semi-core electrons are additionally correlated, but simultaneous two-electron excitations are not involved from the semi-core shells.
3. C: valence and semi-core electrons are correlated at the same footing.

However, an imbalance in the CV scheme, in which the intra $3d$ shell correlation is not taken into account but the N $2s$ shell is normally correlated as valence, was suspected because of the orbital interaction denoted above. To check this suspicion, a set of SCF-reference CPA-4 calculations by the V, CV, and C schemes was carried out for the $^3\Sigma^-$ state, which has less near-degeneracy than does the $^3\Pi$ state. The resulting R_e values for *V*, *CV*, and *C* schemes are 3.91 au, 3.68 au, and 3.83 au, repectively. The bond contraction by the *CV* scheme looks overestimated, and consequently the *V* and *C* schemes were employed for the MRCPA-4 calculations.

In generating singly and doubly excited CSFs, the SCF-type configuration (being the single CSF) and the bonding/anti-bonding doubly excited configuration (also the single CSF) in the CASSCF wavefunction were used as the reference set:

$$^3\Sigma^-(^3A_2) : (1)\sigma_{4s}^2\sigma_b^2\pi_{b(x)}^1\pi_{b(y)}^1, (2)\sigma_b^2 \rightarrow \sigma_{ab}^2$$

$$^3\Pi(^3B_2) : (1)\sigma_{4s}^2\sigma_b^1\pi_{b(x)}^2\pi_{b(y)}^1, (2)\pi_{b(x)}^2 \rightarrow \pi_{ab(x)}^2$$

All possible spin-couplings for each excited configuration were taken in the CSF generation. The highest five ($3 \times a_1$, b_1, and b_2) external MOs were kept unoccupied since these MOs have the radial node in the core region [2]. The lengths of the expansions for the *C* scheme, in which total of 18 electrons were correlated, were 971 570 for $^3\Sigma^-$ and 964 435 for $^3\Pi$. For the $^3\Sigma^-$ state, three CSFs associated with the singly excited configuration of $\sigma_b \rightarrow \sigma_{ab}$ were included as the zeroth-order space to be pre-diagonalized since these CSFs were potentially of an "intruder" type [3–7], although the contribution at the CASSCF stage was small. Thus, the notation of 2R(+1)CPA-4 is used for $^3\Sigma^-$ henceforth. The number of CSFs for 2R(+1) was five. In contrast, all the CSFs of remaining six configurations in CAS-CI were treated in the zeroth-order space for $^3\Pi$, and thus its notation was 2R(+6)CPA-4 (or the dimension of zeroth-order space was 12, the same as the CAS-CI). 2RCI calculations were carried out in parallel for a cross-check purpose. For the $^3\Pi$ state, 3RCI calculations, in which the $\pi_b \rightarrow \pi_{ab}$ singly excited configuration was additionally used for the reference configurations, were also performed, where its expansion length was 2 297 441. Davidson's correction, denoted as $+Q$ [27], was added to CI energies for a remediation of the lack of size consistency.

Values of the bond energy (D_e) for $^3\Sigma^-$ were evaluated in two ways, as was done previously [2]. The first way was the so-called supermolecule (SM) approach, where the state of the dissociation limit was set to the high-spin $^5\Sigma^-$ with a Ga-N distance of 100 au. The second way was due to the sum of separated atom energies (SAE). At the *C* level of calculation, the expansion length for SM was as large as 3 098 797 and we were unfortunately unable to perform the CPA-4 calculation. Thus, only the SAE value was available for the *C*-2R(+1)CPA-4 case, but the difference of that from SM was expected to be small since (MR)CPA-4 has a size consistency [2–7]. A multiplicity-averaged spin-orbit splitting of −0.07 eV for the Ga ($^2P_{1/2}$–$^2P_{3/2}$) atom [28] was corrected for D_e [1, 2]. The atomic masses for Ga and N in the vibrational frequency (ω_e) evaluation were 68.9256 and 14.0067, respectively.

Table 1. Spectroscopic constants for gallium nitride (GaN) in the $^3\Sigma^-$ ground state

Method	D_e (eV)^{a,b,c}	R_e (au)	ω_e (cm^{-1})
2R(+1)	1.11	3.83	477
V			
2RCI	1.76 (1.56)	3.81	506
2RCI + Q	1.85 (1.80)	3.83	494
2R(+1)CPA-4	1.86 (1.88)	3.82	505
C			
2RCI	1.76 (1.22)	3.76	523
2RCI + Q	1.90 (1.69)	3.77	515
2R(+1)CPA-4	(1.95)	3.76	546

[a] A multiplicity-averaged spin-orbit splitting for the Ga atom (−0.07 eV [28]) was taken into account for the present calculations, as in [1, 2]

[b] Calculated D_e in parentheses was due to the "sum of atomic energies" scheme. Refer to text

[c] Total energies are −1977.6087 au for 2R(+1), −1977.8107 au for *V*-2R(+1)CPA-4, and −1978.2413 au for *C*-2R(+1) CPA-4 (at each R_e). Thus, the correlation energies for the *V* and *C* schemes of CPA-4 are 5.50 eV and 17.21 eV, respectively. CI energies are omitted here because of a lack of size consistency

4 Spectroscopic constants of $^3\Sigma^-$ and $^3\Pi$

Table 1 summarizes the spectroscopic constants D_e, R_e, and ω_e for the $^3\Sigma^-$ ground state. In this table, results due to the zeroth-order space of 2R(+1) in CPA-4 are also included. D_e results are first focused on. One can see immediately that the difference between the SM and SAE (in parentheses) approaches is reasonably small for CPA-4, but the difference is unacceptable for CI even with Davidson's correction at the *C* level of treatment. This is a quite similar situation to the previous case of GaF [2]. Size consistency is an essential requirement.

Through the introduction of correlations, D_e is increased from the 1.11 eV which has been calculated by the zeroth-order treatment of 2R(+1). This illustrates the importance of the differential correlation energy for the estimation of bond formation. Even by the *V* scheme, the increment is as large as ~0.7 eV. Introduction of the 3*d* electron correlation through *C*-2R(+1)CPA-4 adds 0.07 eV according to the SAE approach and provides the value 1.95 eV as the best D_e prediction for the GaN molecule. Balasubramanian [15] reported 1.9 eV for the isovalent GaAs molecule by the CASSCF procedure followed by second-order MRCI (so-called SOCI), where he used a couple of special corrections including Meier's value of 0.2 eV [16] for the 3*d* correlations of both Ga and As atoms. For AlN, the D_e value was calculated to be 2.3 eV [16] by the MRCI+Q level for the $^3\Sigma^-$ state [19]. The predicted D_e of GaN would be comparable to those of GaAs and AlN.

R_e and ω_e values present an impact of correlation contribution of semi-core 3*d* electrons. By the *C*-2R(+1)CPA-4 calculation, R_e is contracted by −0.06 au and ω_e is increased by 41 cm^{-1}. As the best results, 3.76 au for R_e and 546 cm^{-1} for ω_e are predicted. The *C*-2RCI+Q procedure provides a preferable contraction for R_e but does not work for ω_e. An inherently size-consistent method is highly required for such as the present type of theoretical investigations.

At the R_e by *C*-2R(+1)CPA-4, the dipole moment is calculated to be 1.69 D with the direction of Ga$^{\delta+}$-N$^{\delta-}$. The σ_b orbital is being characterized as $\lambda 4p + 2p$ but this polarity of charge is somewhat compensated by delocalizations of two N $2p\pi$ electrons toward the Ga $4p\pi$ side in π_b MOs. A similar charge compensation to this was found in the GaF case [2].

The occupation numbers of *C*-2R(+1) CPA-4 resulting NOs are 1.89 for the σ_b type and 0.06 for σ_{ab}, where the weight of the zeroth-order space is 84%. The necessity of the MR scheme for GaN is well demonstrated here. This situation in GaN is quire different from the GaH and GaF cases, in which no tangible near-degeneracy was observed for the σ bonding [1, 2].

Now, the π-bonding $^3\Pi$ state is discussed. Table 2 summarizes spectroscopic constants for this state. Instead of D_e in Table 1 for $^3\Sigma^-$, T_e values are shown in this table. One can observe a relation between T_e and R_e, depending on the treatment of the correlation. The

Table 2. Spectroscopic constants for GaN in the $^3\Pi$ first excited state

Method	T_e (eV)	R_e (au)	ω_e (cm^{-1})
V			
2RCI	0.27	3.61	591
2RCI + Q	0.12	3.62	584
3RCI	0.14	3.60	600
3RCI + Q	−0.03	3.61	597
2R(+6)CPA-4	0.29	3.64	583
C			
2RCI	0.34	3.53	607
2RCI + Q	0.20	3.51	605
3RCI	0.20	3.49	618
3RCI + Q	0.09	3.49	616
2R(+6)CPA-4	0.50	3.57	637

C-2R(+6)CPA-4 calculation provides 0.5 eV as the best T_e prediction at its R_e of 3.57 au. By the *V* scheme, the separation is only 0.29 eV at R_e of 3.64 au. The introduction of semi-core 3*d* correlation leads to the contraction of −0.07 au for R_e and the increase of 54 cm^{-1}. The amount of these numerical shifts provided by the *C* scheme is similar to the $^3\Sigma^-$ state (refer to Table 1). CI results are again found to be inferior to CPA-4, even at the 3R level of reference setting. T_e estimates with +Q correction seem to be too small or overshot.

The occupation numbers of NOs by *C*-2R(+6)CPA-4 are 1.88 for π_b and 0.1 for π_{ab} at R_e, where the weight of the zeroth-order space is 83%. The larger occupation in π_{ab} than σ_{ab} for the $^3\Sigma^-$ state (recall the value of 0.06) clearly illustrates that there is the more severe near-degeneracy in the π bond. The dipole moment is calculated to be 1.61 D for the $^3\Pi$ state.

According to the *C* scheme CPA-4 calculations, the $^3\Pi$ states has the shorter R_e by −0.19 au and the larger ω_e by +91 cm^{-1} than those of the $^3\Sigma^-$ state. The shorter R_e for $^3\Pi$ reflects the fact that the π bonding requires the closer Ga-N distance for the better overlap between 4*p*π and 2*p*π AOs owing to a symmetrical reason. The higher ω_e for $^3\Pi$ is in accord with this nature. Higher frequencies for the π bonding state than σ bonding case have been found previously [13–16, 19]. The transition of $^3\Sigma^- \rightarrow {}^3\Pi$ is of a dipole-allowed type in the infrared region. However, the (0, 0) vibrational transition is expected to be weak because of a sizable difference in R_e, as was pointed out by Meier et al. [16] for the GaAs molecule based on the evaluation of Franck-Condon factors. Such an analysis, which should require a wide range of potential energy curves and the vibrational wavefunctions for GaN, may be a future subject.

5 Summary

Spectroscopic constants of the GaN diatomic molecule were predicted, based on MRCPA-4 calculations in which both the near-degeneracy in valence bonding and the correlation among Ga 3*d* semi-core electrons were taken into account. The ground state was revealed to be the σ-bonding $^3\Sigma^-$ state. Its D_e value was evaluated to be 1.95 eV. R_e and ω_e were 3.76 au and 546 cm^{-1}, respectively. The π-bonding $^3\Pi$ state was shown to be low lying with a T_e of 0.5 eV. A considerably shorter R_e of 3.57 au was obtained for $^3\Pi$, indicating the need for a closer distance for π bonding.

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