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RESEACH ARTICLE

Core - valence correlation effects in the ground and low - lying excited states of GaN

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We present careful analysis of the accuracy of molecular properties of the GaN molecule calculated by the Coupled Cluster CCSD(T) method including the core-valence correlation effects. We demonstrate that calculations of the core-valence correlation effects with basis sets which were optimized considering just valence electrons of the gallium atom lead to unreliable results. Our objective is finding the relation between the accuracy and the oversimplification due to the use of aug-cc-pVXZ basis sets when 3d and eventually also 3s3p electrons are correlated with these basis sets, having in mind calculations of larger systems. We observe the oscillatory behaviour of molecular properties with increasing cardinal basis set number X in the aug-cc-pVXZ series. This is main deficiency of this more economical basis set. Extrapolation to the complete basis set limit with this series is only possible starting with the aug-cc-pVQZ basis. Regular behaviour with increasing X show results with the aug-cc-pCVXZ series. Reasonable molecular **properties are provided by the ANO-RCC** basis sets with 3d¹⁰4s²4p¹ correlated electrons of Ga.

Keywords: GaN molecular properties; excited states; core correlation effects; CCSD(T), CASPT2, aug-cc-pVXZ and aug-cc-pCVXZ basis sets

This paper is dedicated to Professor Hans-Joachim Werner at the occasion of his 60th birthday as the appreciation of his outstanding contribution to the developments in the field of quantum chemistry.

1. Introduction

Saying that for reasonably accurate calculations of molecules containing a IIIA element the $(n-1)d$ electrons must be correlated, along with three ns^2np^1 valence electrons, means nothing new [1–4]. Less frequently is stressed that this should be accompanied by choosing a basis set, which is constructed having in mind correlation of deeper shells of a IIIA element [1, 2]. In our recent paper [5] we have correlated at least $(n-1)d^{10}ns^2np^1$ electrons of gallium (or indium) and five $2s^22p^3$ valence electrons of the nitrogen atom in calculations of molecular properties of the GaN and InN dimers. With the common aug-cc-pVXZ basis set series (X=T, Q,

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or 5) [6] we have observed unexpectedly large basis set superposition error (BSSE) [7] for some reaction energies corresponding to the breakdown of the $(\text{GaN})_2$ or $(\text{InN})_2$ dimer. This is a clear signal of the inadequacy of the basis set used for such calculations. Similar indication of errors due to the use of inappropriate basis set was carefully analyzed in calculations of GaN and other strongly bound systems, like GaNGa, by Tzeli and Tsekouras [2]. For molecules containing Ga to Kr elements DeYonker, Peterson and Wilson [1] have constructed and optimized the family of core - valence aug-cc-pCVXZ sets to correlate the $3s3p3d$ shell along with the valence $4s4p$ electrons within the spin-free Douglas-Kroll-Hess (DKH) relativistic approximation [8]. Such basis sets should be used for the treatment of the IIIA element containing molecules when correlating more than just valence ns^2np^1 electrons of a metal element.

Clearly, aug-cc-pCVXZ basis sets are much larger than their precursors, the correlation consistent polarized valence aug-cc-pVXZ basis set family created by Wilson *et.al.* [6]. Combining large basis sets and large number of correlated electrons becomes prohibitively demanding when Coupled Cluster CCSD(T) or other highly sophisticated methods are used for calculations of compounds containing several Ga or other IIIA group elements. Therefore, for pragmatic reasons, it is tempting to correlate $(n-1)d^{10}ns^2np^1$ or more core-valence electrons, yet using a simpler aug-cc-pVXZ basis. However, aug-cc-pVXZ basis sets for Ga were constructed considering the correlation of the $4s^24p^1$ valence shell only. Strictly speaking, correlating more than 3 electrons of a IIIA group element with these basis sets is inappropriate. Intuitively, one may feel that pushing such a basis sets "to do a job" for which they were not constructed, that is, to correlate $(n-1)d^{10}ns^2np^1$ or more electrons, is better than nothing and the error is hopefully small. DeYonker *et. al* [1] have concluded their investigation of this problem saying, "the detrimental effects of correlating the $3s3p3d$ electrons with just the valence aug-cc-pVXZ basis sets are clearly observed". Their observation is based on calculations of spectroscopic properties of the Ga_2 up to Kr_2 molecules in their ground state. Combining this warning with the fact that at least $3d$ electrons must be correlated for accurate (or even semi-accurate results) leaves a small space for a meaningful use of aug-cc-pVXZ basis sets for molecules containing Ga and similar elements. Unfortunately, the necessity of using aug-cc-pCVXZ basis sets may be quite demanding for large scale calculations.

Therefore, we have decided to perform CCSD(T) calculations of properties of the GaN molecule addressing two issues in this paper. The first one is a systematic investigation of the relation between the accuracy and the oversimplification due to using aug-cc-pVXZ basis sets when $3d$ and eventually also $3s3p$ electrons are correlated with these basis sets, having in mind calculations of larger systems. Along with careful consideration of the relation between the way in which the basis set was constructed and the number of correlated electrons, our aim is also presenting accurate CCSD(T) data for selected properties of this molecule. We will focus on first three electronic states, the ground $^3\Sigma^-$ state, and low lying $^3\Pi$ and $^1\Sigma^+$ excited states of GaN. We calculated bond lengths, dissociation and excitation energies, dipole moments and dipole polarizabilities. The electronic configuration for the three states is $\dots(10\sigma)^2(4\pi_x)^1(4\pi_y)^1$, $\dots(10\sigma)^1(4\pi_x)^2(4\pi_y)^1$, and $\dots(10\sigma)^0(4\pi_x)^2(4\pi_y)^2$, respectively. GaN is an important molecule since it is a part of common semiconductor materials widely used in nanotechnology and optoelectronics. Compounds containing GaN received a lot of attention in many experimental and theoretical studies in which molecular clusters [5, 9–12] and simulations of GaN containing surface processes [13, 14] were considered. Unfortunately, there is no experimental study of GaN diatomic at the time. A few theoretical papers

can be found in the literature. The ground state was determined as $^3\Sigma^-$. A qualitative bonding picture of this state was analyzed by Mochizuki and Tanaka [3]. Subsequent studies were presented by Ueno *et al.* [15], Denis and Balasubramanian [4] and recently Tzeli and Tsekouras [2].

We used a series of aug-cc-pVXZ ($X=T, Q, 5$) and aug-cc-pCVXZ ($X=T, Q$, and 5) basis sets correlating three up to 21 electrons of Ga and five up to all seven electrons of the nitrogen atom. In some calculations we have correlated all 31 electrons of Ga, but actually there is no contracted basis set constructed having in mind correlating also inner shell $1s^2 2s^2 2p^6$ electrons of Ga. Therefore we do not present calculations with all 38 electrons correlated for GaN in this paper. By systematic comparison of results with different basis sets and different correlation schemes we tried to reveal inaccuracies when combining a specific basis set with inappropriate number of correlated electrons. All basis sets were constructed having in mind their use within the spin-free Douglas-Kroll-Hess (DKH) relativistic approximation [8].

Along with results using the aug-cc-pVXZ ($X=T, Q, 5$) and aug-cc-pCVXZ basis sets we also present CCSD(T)-DKH calculations with the relativistically constructed ANO-RCC (Atomic Natural Orbitals) basis set [16]. ANO-RCC basis sets for Ga and N were contracted to the size corresponding to the aug-cc-pVQZ basis. The difference is that the aug-cc-pVQZ basis was constructed with correlating only three valence electrons of Ga, whereas the ANO-RCC basis set was developed having in mind correlation of 13 outer shells $3d^{10} 4s^2 4p^1$ electrons of the Ga atom.

2. Computational details

All calculations were carried out with the MOLCAS suite of programs [17]. The CCSD(T) Coupled Cluster method with single and double excitations and perturbative triples [18, 19] with an approximate spin adaptation [20] was employed in all calculations using the Restricted Hartree Fock reference for high spin open-shell states. Our method is similar to the approach developed independently by Knowles, Hampel and Werner [21]. This method leads to energies which are very close to the energies obtained by the rigorous (even if slightly more demanding) method [22] for the spin adaptation. Denominators in perturbatively calculated triples were diagonal Fock-matrix elements [23], see also Refs. [20, 24]. In all calculations we have considered scalar relativistic effects using the second-order spin-free scalar relativistic approach introduced by Douglas, Kroll, and Hess (DKH) [8].

The evaluation of the dipole moment and the parallel zz component of the dipole polarizability was accomplished using the numerical finite field perturbation approach [25]. The strength of the external electric field was 0.001, 0.002, and 0.004 au, respectively. Final dipole moments and dipole polarizabilities were obtained using the numerical derivatives prescription, which allow to remove the higher order terms [26, 27].

Five correlation schemes were used for aug-cc-pVXZ, aug-cc-pCVXZ ($X=T, Q, 5$), and ANO-RCC basis sets. For the gallium atom we correlated 3 valence ($4s^2 4p^1$) electrons, 13 ($3d^{10} 4s^2 4p^1$), 19 ($3p^6 3d^{10} 4s^2 4p^1$) and 21 ($3s^2 3p^6 3d^{10} 4s^2 4p^1$) electrons. These four correlation schemes for Ga were combined with correlating five valence electrons of the nitrogen leading to the total number of 8, 18, 24, or 26 correlated electrons of the three states of GaN. In addition, the ($3s^2 3p^6 3d^{10} 4s^2 4p^1$) correlation scheme of 21 electrons of Ga was combined with correlating all seven electrons of nitrogen, leading to the total number of 28 correlated electrons. Some data, not presented here, were also obtained by correlating all 31 electrons of Ga.

Basis sets used for calculations of molecular properties of GaN molecule differ in

size significantly. This is important for considering the relation between the accuracy and computer demands. One should realize that the worst step in CCSD(T) scales with the number of occupied and virtual orbitals with the factor $N_o^3 N_v^4$. Aug-cc-pVXZ basis has 105 contracted basis functions for $X=T$, 173 for $X=Q$ and 267 for $X=5$, respectively. ANO-RCC was contracted to the size of aug-cc-pVQZ having 173 basis functions. Core-valence basis sets are considerably larger, having 159 functions in the aug-cc-pCVTZ basis set, 279 and 444 basis sets in the aug-cc-pCVQZ and aug-cc-pCV5Z basis sets, respectively. We note that the standard aug-cc-pV5Z and core-valence aug-cc-pCVQZ basis sets contain approximately the same number of basis functions, but were constructed differently.

In order to predict molecular properties more accurately we have estimated the complete basis set limit (CBS) using the $1/X^3$ fit with respect to the basis set cardinal number X [28]. Data from aug-cc-p(C)VXZ series with $X=T, Q, 5$ or $X=Q, 5$ were employed. Dissociation energies were corrected for the basis set superposition error (BSSE) by the usual counterpoise correction [7].

3. Results

Considering the manner adopted for the construction of the aug-cc-pVXZ series, proper number of correlated electrons for GaN with these basis sets would be 8. Proper number of correlated electrons with the aug-cc-pCVXZ series is 28. Results with the aug-cc-pCVXZ series and 28 correlated electrons will be considered as reference numbers for each property. With the ANO-RCC basis set the proper number of correlated electrons is 18. Results with these "proper" contraction schemes are printed in bold in Tables 1 to 4, in which we summarize optimized CCSD(T) bond distances, BSSE corrected dissociation energies and electric properties of the GaN molecule. A transparent view upon the relation between the basis set and the number of correlated electrons is seen in Figure 1 for the excitation energy from the $^3\Sigma^-$ ground state to the $^3\Pi$ state and in Figure 2 for the excitation energy to the $^1\Sigma^+$ state. In Table 5 we present our best results for dissociation and excitation energies, dipole moments and dipole polarizabilities for the three states of GaN with 28 correlated electrons and CBS limits obtained by extrapolations from aug-cc-pCVXZ ($X=T, Q, 5$) basis sets.

3.1. GEOMETRIES

Optimized bond lengths with the aug-cc-pVXZ and ANO-RCC basis sets are presented in Table 1 and results with the aug-cc-pCVXZ series are presented in Table 2. It is immediately clear that results with only 8 correlated valence electrons of GaN in all three states differ significantly, by 0.10 - 0.15 from R_e with 28 correlated electrons and the CBS limit. This holds for the aug-cc-pVXZ, aug-cc-pCVXZ series and also for ANO-RCC basis sets reconfirming the necessity of correlating at least 3d electrons of the Ga atom containing species. To correlate 3p electrons of Ga is needed for more accurate results, remaining core-valence correlation effect is unimportant particularly for excited states. Going deeper beyond the 3d Ga shell with, say, the aug-cc-pCVQZ basis set, optimized values of R_e for the ground and the two excited states of GaN are lying within the relatively narrow interval of 0.002 - 0.006 bohr with 18 up to 26 correlated electrons. With the valence-only aug-cc-pVQZ basis, this interval is much larger, 0.015–0.025 Bohr leading to exaggerated importance of the core-valence correlation effects. With all aug-cc-pVXZ bases R_e decreases upon correlating more than $3d^{10}4s^24p^1$ electrons of Ga, in con-

trast to the trend with the aug-cc-pCVXZ series. Since aug-cc-pVXZ basis sets are not constructed for treating the core–valence correlation, increased computational effort leads in fact to inferior results.

CBS limits from aug-cc-pCVXZ basis sets with 18 correlated electrons ($3d^{10}4s^24p^1$ electrons of Ga) do not change significantly upon considering also the Ga $3s^23p^6$ shell. Dominating core–valence correlation arises from the 3d correlation effect. The nitrogen core correlation effect can be estimated by comparing results with 26 and 28 correlated electrons. It amounts 0.003 - 0.002 Bohr for the ground state and both excited states. The convergence of R_e toward the CBS limit with the aug-cc-pCVXZ series is smooth. However, with the smallest aug-cc-pCVTZ is R_e overestimated by about 0.03 bohr (more for the ground state than for excited states). Accidentally, the (Q,5) CBS limit as obtained from aug-cc-pVQZ and aug-cc-pV5Z basis sets agrees relatively well with the aug-cc-pCVXZ CBS limit with 24–28 correlated electrons. This is an example of a good result for a wrong reason. The basis set dependence of R_e on the principal number X (X=T, Q, and 5) is oscillatory for aug-cc-pVXZ bases, with no control of accuracy, in contrast to the aug-cc-pCVXZ series, which is smooth. Should aug-cc-pVXZ basis sets be used, it is imperative to avoid the smallest member of the series, the aug-cc-pVTZ basis, since the (T,Q,5) extrapolated value differs from the (Q,5) CBS limit by up to 0.04 bohr. With aug-cc-pCVXZ basis sets the three-point and the two-point CBS limits agree excellently.

When thinking about the most economic way of obtaining acceptably accurate R_e with a single basis set, one should be satisfied with correlating just 18 electrons in CCSD(T). For all three states of GaN good agreement with our best CBS limit is obtained with the ANO-RCC basis. It clearly outperforms the aug-cc-pVQZ basis set **which has smaller number of primitives but the same number of contracted basis functions**. Due to the oscillatory behaviour of R_e calculated with aug-cc-pVXZ basis sets we do not recommend using aug-cc-pVTZ basis for Ga containing compounds, even if, paradoxically, result with 28 correlated electrons (3.748 bohr, as compared with the CBS limit, 3.750 bohr) is not bad, clearly thanks to the error cancellations. However, since computer demands of CCSD(T) calculations increase with the number of correlated electrons with the power of 4 the advantage of using the small basis set is diminished. Relatively small is the aug-cc-pCVTZ basis set, but due to missing cancellation of errors results are no better than with ANO-RCC or aug-cc-pVQZ basis sets. Aug-cc-pCVQZ basis set is larger but results are more reliable.

3.2. DISSOCIATION ENERGIES

The performance of the valence-only aug-cc-pVQZ, aug-cc-pCVQZ and ANO-RCC basis sets in calculations of electronic adiabatic dissociation energies (D_e) is presented in Table 3. Geometries were taken from Tables 1 and 2. The ground state $X^3\Sigma^-$ and the first excited state $A^3\Pi$ dissociate to Ga $^2P + N^4S$, the second excited $a^1\Sigma^+$ state dissociates via the Ga $^2P + N^2D$ channel.

Analyzing data in Table 3 we observe, first, that correlating just eight valence electrons provides D_e s which are underestimated by about 0.06, 0.1, and 0.23 eV for the ground state and $A^3\Pi$ and $a^1\Sigma^+$ excited states in comparison with calculations with 18 to 28 correlated electrons. Second, upon correlating 18 to 28 electrons all values lie within relatively narrow interval of about 0.02 - 0.03 eV. This is a small value considering other effects which affect the accuracy of calculated D_e . In light of the discussion on proper use of basis sets and the number of correlated electrons for calculations of the GaN bond length, dissociation energies of all three states

agree very well, to within 0.02 eV or even better for aug-cc-pVQZ, aug-cc-pCVQZ, and ANO-RCC basis sets. Thus, somewhat surprisingly, there are no remarkable differences in the performance of the three basis sets in CCSD(T) calculations of D_e . This holds for all three states considered in this work. Yet, there is an indication signaling inferior performance of the aug-cc-pVQZ basis set. Good results with this basis are accompanied by quite large BSSE (see last three columns of Table 3), 0.1 up to 0.4 eV for the three states. The only exception is D_e calculated with 8 correlated electrons. Large BSSE compensates the deficiency of the insufficient description of the deeper electron shells of the Ga atom with the aug-cc-pVQZ basis set. BSSE is small for ano-rcc basis when we correlate 3d electrons of gallium (which is exactly what it was constructed for). In case of aug-cc-pCVQZ basis BSSE is order of magnitude smaller than with the aug-cc-pVQZ basis for all correlation schemes. Exaggerated importance of the BSSE correction when the basis set is not appropriate for the number of electrons which are correlated was also observed in calculations of D_e for the ground state of GaN and for Ga_2 by Tzeli and Tsekouras [2]. Their CCSD(T) CBS limit for D_e of the ground state (2.12 eV) obtained with 18 correlated electrons employing small-core relativistic pseudopotentials basis agrees reasonably well with our best value, 2.140 eV (Table 5).

As mentioned above, the second excited $a^1\Sigma^+$ state dissociates via the $\text{Ga } ^2P + \text{N } ^2D$ channel. Since the doublet state of the nitrogen atom shows a multireference character which is accompanied by high excitation amplitudes (up to 0.28) in the single reference CCSD calculation, results with the single-determinant reference CCSD(T) method may not be conclusive due to quasidegeneracy effects. To ensure that our conclusions concerning the performance of differently constructed basis sets are not plagued by quasidegeneracy effects, we used the CASPT2 method for evaluation of dissociation energies of all three electronic states along with CCSD(T). The active space contains 8 valence electrons in 8 active orbitals (4s4p of the gallium atom and 2s2p orbitals of the nitrogen atom). CASPT2 dissociation energies with 26 correlated electrons using aug-cc-pVQZ, aug-cc-pCVQZ and ANO-RCC basis sets are presented in Table 3. Comparison of CCSD(T) and CASPT2 dissociation energies with the series of aug-cc-pCVXZ basis sets ($X=T, Q$, and 5) is shown in Table 5 for 28 correlated electrons. For the ground $X^3\Sigma^-$ state CCSD(T) and CASPT2 results differ by less than 0.1 eV, CASPT2 $D_{e,s}$ values being slightly higher than CCSD(T) dissociation energies. Similarly, CASPT2 dissociation energies of the first $A^3\Pi$ excited state are higher than CCSD(T) ones, this time by 0.12 to 0.17 eV. Conversely, for the $a^1\Sigma^+$ state is the CASPT2 dissociation energy lower than the CCSD(T) energy. This reflects the overestimated energy of the nitrogen 2D state by CCSD(T). The importance of triples in CCSD(T) can be determined by comparing CCSD(T) and CCSD dissociation energies in Table 5. For the ground state this contribution is relatively small, 0.1 eV, but for the $A^3\Pi$ and the $a^1\Sigma^+$ states it increases up to 0.2 and almost 0.5 eV, respectively. Therefore, comparisons of CCSD(T), CCSD, and CASPT2 data demonstrate that details of the treatment of correlation effects matter. Concerning BSSE, conclusions from CASPT2 and CCSD(T) data for D_e are completely the same: BSSE is much larger for aug-cc-pVQZ basis set than for the aug-cc-pCVQZ basis. With CASPT2 it is larger than with CCSD(T) with all three bases.

3.3. DIPOLE MOMENTS AND DIPOLE POLARIZABILITIES

The performance of aug-cc-pVQZ, aug-cc-pCVQZ and ANO-RCC basis sets in calculations of dipole moments and parallel dipole polarizabilities with 8 to 28 correlated electrons is documented in Table 4. Optimized internuclear distances

are taken from Tables 1 and 2 for each particular correlation scheme and the basis set. Originally, we expected that dipole moments and polarizabilities will be very sensitive to the number of correlated electrons and the basis set. It appears, however, that the sensitivity of electric properties to the basis set is not dramatic. For example, considering 26 correlated electrons for the ground state with the aug-cc-pVQZ basis set (inappropriate basis for this calculation) the dipole moment is 0.719 a.u. It differs by 9.1 % from the aug-cc-pCVQZ basis set result. Note that ANO-RCC result differs from this reference number much less, by 3.3 %. The basis set dependence for both dipole moment and polarizability with the aug-cc-pCVXZ series and 28 correlated electrons is even smaller, as expected, see Table 5. Aside from data obtained with 8 correlated electrons, dipole moments and dipole polarizabilities are insensitive also to the number of correlated electrons. With all basis sets the CCSD(T) dipole moments of GaN with 18-26 correlated electrons lie in the interval narrower than 0.02 a.u. for all states. Core correlation effect due to correlating inner shell 1s electrons of nitrogen is 0.005 a.u. for the $a^1\Sigma^+$ state and even smaller for the ground and the $A^3\Pi$ excited states. Analogous insensitivity holds for the parallel polarizability.

3.4. EXCITATION ENERGIES

Adiabatic CCSD(T)-DKH excitation energies T_e from the ground $X^3\Sigma^-$ state to the first two excited $A^3\Pi$ and $a^1\Sigma^+$ states, respectively, are much more sensitive to the selection of the basis set and proper correlation scheme than are other properties. Nevertheless, when discussing details of the basis set effects we should realize that the energy gap between the ground $X^3\Sigma^-$ state and the $A^3\Pi$ excited state is quite small.

For the two states with 8-28 correlated electrons **the basis set dependence of T_e is transparently** demonstrated in Figures 1 and 2, respectively. On the left hand side we present the series aug-cc-pVXZ (X= T, Q, and 5), supplemented with ANO-RCC results. On the right hand side there are excitation energies with the aug-cc-pCVXZ series. For both series we also present CBS limits. Not much discussion is needed for results with 8 correlated electrons. Excitation energies with all basis sets are quite similar, the basis set dependence for both aug-cc-pVXZ and aug-cc-pCVXZ series is smooth, but excitation energies are much too high. More interesting are results with 18-28 electrons. As a curiosity we note that T_e with the smallest aug-cc-pVTZ basis and 18 correlated electrons agrees very well with the CBS limit calculated from much more demanding aug-cc-pCVXZ series, 0.104 and 0.747 eV for $A^3\Pi$ and $a^1\Sigma^+$ states, respectively. Typically, this is a good result for the wrong reason. Upon correlating 26 or 28 electrons and extending the aug-cc-pVTZ basis to aug-cc-pVQZ the excitation energy of the $A^3\Pi$ state diminishes to about 0.04 eV. Extrapolating to the CBS limit with these two basis sets we would obtain completely misleading result, 0.007 eV with 28 correlated electrons. This may lead to some doubts about the state ordering in GaN. We remind that there was a long lasting discussion about the ordering of states for valence isoelectronic BN and AlN molecules stressing the importance of proper handling of electron correlation effects for these species [29, 30]. When calculating the CBS limit using smaller aug-cc-pVXZ series one should be careful since the behavior of T_e with respect to the cardinal number X is oscillatory for both excited states. In any case, the smallest aug-cc-pVTZ must be avoided in the extrapolation to the CBS limit **when core electrons are correlated**. In contrast, T_e is much less sensitive to the cardinal number in the aug-cc-pCVXZ series, it is also almost insensitive to the number of correlated electrons, the basis

set dependence is smooth and thus results are much more reliable. The problem is the size of aug-cc-pCVXZ bases. The largest aug-cc-pCV5Z basis set with 444 basis functions is no problem for the CCSD(T) calculation of a single GaN molecule but would be demanding or intractable for dimers or larger complexes. For the sole calculation of T_e a good choice is using the ANO-RCC basis set. Another good candidate for a single-shot calculation would be the aug-cc-pCVQZ basis set (279 basis functions). For the sake of saving the computer time with this basis set it is satisfactory to correlate only 18 electrons (even if it was constructed having in mind 28 correlated electrons for GaN). Much larger error for both excited states in comparison with the CBS limit from Table 5, is obtained with, e.g., the aug-cc-pV5Z basis set (267 basis functions).

For accurate calculation of excitation energies of GaN and other IIIA element molecules it is necessary to consider carefully also the treatment of the electron correlation. Starting from InN one should also take care of the spin-orbit coupling [31]. We observe (Table 5) that T_e for the $A^3\Pi$ state with the CCSD method is higher than with CCSD(T) by about 0.1 eV and even more (by as much as 0.5 eV) for the $a^1\Sigma^+$ state. Therefore, triples contribute significantly. At the same time, with CASPT2(8,8) are excitation energies for the $A^3\Pi$ state lower than CCSD(T) energies by about 0.06-0.08 eV with aug-cc-pCVXZ basis sets. Finally, users of the valence-only aug-cc-pVXZ basis sets should have been alert to the possibility of the reversed order of stabilities of states with CASPT2. With the aug-cc-pVQZ basis set T_e of the $A^3\Pi$ state decreases with the number of correlated electrons from 0.154 eV for 8 electrons correlated even up to the negative value of -0.004 eV for 26 electrons correlated.

3.5. CONCLUSIONS

Our best CCSD(T) DKH results for dissociation and excitation energies, dipole moments and dipole polarizabilities of the $^3\Sigma^-$, $^3\Pi$ and $^1\Sigma^+$ states of the GaN molecule are summarized in Table 5. All results include the scalar relativistic effects and the core-valence electron correlation effects treated with the aug-cc-pCVXZ basis set series. Our CBS limits can be considered as benchmark results for properties of the low-lying states of GaN. The CCSD(T) DKH dissociation energy of all three states of GaN should be supplemented by the spin-orbit contribution. According to recent work of Shirai [33] the value for the $^2P_{3/2} - ^2P_{1/2}$ splitting of the Ga atom is 829 cm^{-1} . The spin-orbit splitting for the $^3\Sigma^-$ state of the GaN molecule is negligible [4, 32]. Final best estimate of D_e for the ground $^3\Sigma^-$ state is 2.072 eV. Our CCSD(T) DKH dissociation energy as presented in Table 5 agrees reasonably well with value (2.016 eV) published by Denis and Balasubramanian [4]. Along with CCSD(T) they employed also the MRSDCI method. Similarly as it follows from our CASPT2 and CCSD(T) results, MRSDCI method predicts a smaller separation between the $^3\Sigma^-$ and the $^3\Pi$ states, 532 cm^{-1} in comparison with CCSD(T) (857 cm^{-1}). Even if they do not provide the effect of the basis set in relation to the core-valence correlation their results are in qualitative agreement with our conclusions. Both CCSD(T) and MRSDCI methodologies indicate that the ground state of GaN is $^3\Sigma^-$. Our results also compare very well with more recent results by Tzeli and Tsekouras [2]. These authors studied several gallium and nitrogen containing molecules including the $X^3\Sigma^-$ state of GaN. They correlated 8 and 18 electrons, respectively, using small-core pseudopotentials and various basis sets. The difference between our best geometries and their results for the ground state is only 0.001 Bohr, dissociation energies differ by only 0.02 eV. General conclusions and trends concerning the

performance of aug-cc-pVXZ and aug-cc-pCVXZ basis sets (with X going up to quintuple zeta for both series in the present study) in accurate calculations of these properties of the GaN ground $X^3\Sigma^-$ state are the same. These results are supplemented in this paper by correlating deeper shells of GaN and its low-lying excited states. It appears that excitation energies are most sensitive to proper selection of the basis set as used with different correlation schemes. Our excitation energy for the $A^3\Pi$ state agrees reasonably well with the value published by Denis and Balasubramanian [4], 0.106 eV. However, their value for the $a^1\Sigma^+$ state is overestimated in comparison with our CBS limit (Table 5) by 0.05 eV. This state is more sensitive to basis set effects. Concerning electric properties, we were only able to compare electric dipole moments from the work of Denis and Balasubramanian, obtained by the multireference MRSDCI method finding the differences from our results of about 0.1 a.u. for the three states.

Our systematic investigation of the accuracy, reliability and efficiency for calculations of molecular properties of GaN as a typical species containing a IIIA element leads us to several conclusions on the use of differently constructed basis sets for the treatment of the core-correlation effects. Clearly, it would be advantageous to use relatively smaller aug-cc-pVXZ basis sets for considering the core-valence correlation effects. These basis sets are usually flexible enough in many applications and are smaller than their aug-cc-pCVXZ counterparts. Clearly, some data obtained with these basis sets agree with the CBS limit quite well. However, we were unable to obtain good results in a systematic and controlled manner. Simply, these basis sets were not constructed for core-valence correlations. Yet, considering at least $3d$ electrons for such species is inevitable. In light of this fact and the unreliable performance of the valence aug-cc-pVXZ basis sets when correlating deeper shells of Ga we see little space for using these basis sets as a predictive tool for properties of molecules containing these atoms. Main obstacle is our finding that molecular properties calculated with aug-cc-pVXZ basis sets suffer from the oscillatory behavior with increasing cardinal number. Smaller members of the series, as the aug-cc-pVTZ basis set, should be avoided in any extrapolations to the CBS limit **when core electrons are correlated**. Then the advantage of its relatively smaller size is lost. For larger-scale calculations of IIIA elements compounds we would prefer smaller members of the aug-cc-pCVXZ series. A typical example is the aug-cc-pCVQZ basis set (279 basis functions) which mostly outperforms the aug-cc-pV5Z basis with 267 basis functions. Large number of virtuals can be circumvented by using the truncated space obtained by the OVOS (Optimized Virtual Orbital Space) technique [34]. Utilizing the fact that for virtually all properties calculated in this paper the effect of core valence electrons beyond $3d$ was relatively small we can restrict ourselves just to these electrons. For a single basis set calculation very good compromise between the accuracy and efficiency offer the ANO-RCC basis sets.

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Table 1. Bond lengths (Bohr) of the $^3\Sigma^-$, $^3\Pi$ and $^1\Sigma^+$ electronic state of GaN molecule obtained at the CCSD(T) DKH level employing series of valence basis sets with ANO-RCC basis set and usig 5 correlation schemes.

State	No. of corr. el.	Basis set and its size				Extrapolation	
		ano-rcc ^a 173	aug-cc-pVTZ 105	aug-cc-pVQZ 173	aug-cc-pV5Z 267	(T,Q,5)	(Q,5)
$X - ^3\Sigma^-$	8	3.858	3.874	3.863	3.860	3.856	3.857
	18	3.757	3.766	3.733	3.733	3.719	3.733
	24	3.755	3.760	3.716	3.730	3.710	3.745
	26	3.750	3.754	3.708	3.725	3.704	3.743
	28	3.738	3.748	3.704	3.722	3.701	3.741
$A - ^3\Pi$	8	3.613	3.629	3.620	3.617	3.614	3.614
	18	3.485	3.501	3.467	3.462	3.448	3.457
	24	3.484	3.502	3.452	3.460	3.438	3.468
	26	3.481	3.498	3.444	3.456	3.432	3.469
	28	3.472	3.493	3.441	3.453	3.430	3.466
$a - ^1\Sigma^+$	8	3.323	3.338	3.331	3.327	3.325	3.323
	18	3.206	3.229	3.201	3.194	3.183	3.187
	24	3.203	3.227	3.190	3.191	3.175	3.192
	26	3.202	3.220	3.186	3.190	3.175	3.194
	28	3.196	3.217	3.184	3.187	3.173	3.190

^a - basis set was contracted to size aug-cc-pVQZ basis set.

Table 2. Bond lengths (Bohr) of the $^3\Sigma^-$, $^3\Pi$ and $^1\Sigma^+$ electronic state of GaN molecule obtained at CCSD(T) DKH level employing series of core - valence basis sets and usig 5 correlation schemes.

State	No. of corr. el.	Basis set and its size			Extrapolation	
		aug-cc-pCVTZ 159	aug-cc-pCVQZ 279	aug-cc-pCV5Z 444	(T,Q,5)	(Q,5)
$X - ^3\Sigma^-$	8	3.866	3.858	3.857	3.854	3.856
	18	3.781	3.762	3.755	3.748	3.748
	24	3.788	3.768	3.761	3.754	3.754
	26	3.787	3.767	3.760	3.753	3.753
	28	3.784	3.764	3.757	3.750	3.750
$A - ^3\Pi$	8	3.621	3.614	3.613	3.610	3.612
	18	3.508	3.491	3.484	3.478	3.477
	24	3.515	3.497	3.489	3.482	3.481
	26	3.514	3.496	3.489	3.482	3.482
	28	3.512	3.494	3.487	3.480	3.480
$a - ^1\Sigma^+$	8	3.328	3.323	3.322	3.320	3.321
	18	3.221	3.209	3.204	3.200	3.199
	24	3.223	3.210	3.205	3.200	3.200
	26	3.224	3.211	3.206	3.201	3.201
	28	3.222	3.209	3.204	3.199	3.199

Table 3. CCSD(T)-DKH BSSE corrected dissociation energies (eV) and BSSE (eV) of $^3\Sigma^-$, $^3\Pi$ and $^1\Sigma^+$ electronic states of GaN employing various basis sets. Geometries of GaN are taken from Tables 1 and 2. Data in parenthesis with 26 correlated electrons were calculated using the CASPT2(8,8) method.

	No. corr. electrons	Dissociation energies (eV)				BSSE (eV)	
		aug-cc-pVQZ	aug-cc-pCVQZ	ano-rcc ^a	aug-cc-pVQZ	aug-cc-pCVQZ	ano-rcc ^a
X - $^3\Sigma^-$	8	1.999	2.009	2.002	0.007	0.005	0.007
	18	2.062	2.071	2.065	0.133	0.015	0.045
	24	2.048	2.061	2.055	0.198	0.018	0.104
	26	2.050 (2.156)	2.064 (2.146)	2.058 (2.147)	0.220 (0.258)	0.018 (0.037)	0.132 (0.145)
	28	2.051	2.065	2.059	0.230	0.019	0.217
A - $^3\Pi$	8	1.824	1.832	1.827	0.008	0.006	0.008
	18	1.949	1.959	1.956	0.173	0.018	0.051
	24	1.933	1.946	1.944	0.264	0.022	0.118
	26	1.934 (2.058)	1.949 (2.105)	1.947 (2.113)	0.294 (0.359)	0.023 (0.042)	0.150 (0.162)
	28	1.935	1.949	1.948	0.305	0.023	0.244
a - $^1\Sigma^+$	8	3.733	3.750	3.751	0.010	0.008	0.010
	18	3.960	3.966	3.972	0.221	0.024	0.060
	24	3.925	3.932	3.939	0.345	0.028	0.137
	26	3.934 (3.749)	3.944 (3.788)	3.951 (3.811)	0.384 (0.461)	0.029 (0.051)	0.173 (0.182)
	28	3.955	3.970	3.974	0.397	0.030	0.276

^a - basis set was contracted to size aug-cc-pVQZ basis set.

^b - dissociation products were 2P Ga and 4S N.

^c - dissociation products were 2P Ga and 2D N.

Table 4. CCSD(T)-DKH dipole moments (a.u.) and parallel dipole polarizabilities (a.u.) of the $^3\Sigma^-$, $^3\Pi$ and $^1\Sigma^+$ electronic states of the GaN molecule with aug-cc-pVQZ, aug-cc-pCVQZ and ANO-RCC basis sets and 8-28 correlated electrons. Geometries taken from Tables 1 and 2.

	No. corr. electrons	Dipole moments (a.u.)			Polarizability (a.u.)		
		aug-cc-pVQZ	aug-cc-pCVQZ	ano-rcc ^a	aug-cc-pVQZ	aug-cc-pCVQZ	ano-rcc ^a
X - $^3\Sigma^-$	8	0.823	0.821	0.812	56.85	56.69	55.34
	18	0.735	0.780	0.767	53.45	53.98	52.62
	24	0.732	0.799	0.776	53.14	54.20	52.60
	26	0.719	0.791	0.765	52.95	54.17	52.50
	28	0.719	0.793	0.759	52.74	53.97	52.11
A - $^3\Pi$	8	1.131	1.127	1.117	60.56	60.53	59.53
	18	1.061	1.075	1.063	58.13	57.53	56.52
	24	1.060	1.083	1.066	57.76	57.14	56.09
	26	1.053	1.079	1.061	57.95	57.38	56.33
	28	1.054	1.081	1.059	57.91	57.30	56.26
a - $^1\Sigma^+$	8	1.662	1.670	1.659	59.69	59.61	58.31
	18	1.538	1.542	1.531	54.03	54.01	52.95
	24	1.541	1.546	1.531	53.85	53.98	52.84
	26	1.539	1.546	1.531	53.84	54.06	52.90
	28	1.542	1.551	1.534	53.77	53.97	52.76

^a - basis set was contracted to size aug-cc-pVQZ basis set.

Table 5. Excitation energies (eV), BSSE corrected dissociation energies^a (eV), dipole moments (a.u.) and polarizabilities (a.u.) of first three states of the GaN molecule obtained at CCSD(T) DKH level using aug-cc-pCVXZ (X=T,Q,5) basis sets and correlating 28 electrons. Two extrapolation schemes employ the three-point aug-cc-pCVXZ (X=T,Q,5) data (the TQ5 extrapolation) and the two-point aug-cc-pCVXZ (X=Q,5) data (the Q5 extrapolation). Geometries used are the (Q,5) extrapolated values from Table 2. Numbers in parentheses are CASPT2(8,8) results, see text.

State	Property	Basis set			Extrapolation	
		aug-cc-pCVTZ	aug-cc-pCVQZ	aug-cc-pCV5Z	(T,Q,5)	(Q,5)
$X - ^3 \Sigma^-$	D_e	1.960(2.023)	2.064(2.147)	2.101(2.199)	2.140(2.244)	2.140(2.254)
	$D_e(CCSD)$	1.836	1.933	1.966		
	μ_z	0.773	0.780	0.781	0.784	0.782
	α_{zz}	54.23	53.63	53.42	53.20	53.20
	α_{xx}	50.72 ^b	49.74 ^b			
$A - ^3 \Pi$	T_e	0.122(0.063)	0.112(0.038)	0.108(0.030)	0.104	0.104
	$T_e(CCSD)$	0.221	0.214	0.212		
	D_e	1.827(1.934)	1.949(2.103)	1.991(2.155)	2.037(2.219)	2.035(2.210)
	$D_e(CCSD)$	1.606	1.715	1.753		
	μ_z	1.065	1.074 ^b	1.076 ^b	1.080	1.078
	α_{zz}	57.48	57.24 ^b	57.06 ^b	56.98	56.87
$a - ^1 \Sigma^+$	T_e	0.829(0.752)	0.780(0.702)	0.764(0.686)	0.746	0.747
	$T_e(CCSD)$	1.308	1.274	1.262		
	D_e	3.833(3.550)	3.969(3.793)	4.015(3.835)	4.066(3.931)	4.063(3.879)
	$D_e(CCSD)$	3.391	3.502	3.539		
	μ_z	1.542	1.547	1.548	1.550	1.549
	α_{zz}	54.16	53.81	53.63	53.51	53.44

^a - spin-orbit correction for Ga ²P is 0.068 eV.

^b - used field strength 0.002 0.004 and 0.008.

Figure 1. CCSD(T) DKH excitation energies for GaN A $^3\Pi$ state. The left hand side: Series of valence aug-cc-pVXZ basis sets, with empty symbols represening ANO-RCC basis set contracted to the size of the aug-cc-pVQZ basis. Right hand side: series of core-valence aug-cc-pCVXZ basis sets.

Figure 2. CCSD(T) DKH excitation energies for GaN a $^1\Sigma^+$ state. The left hand side: Series of valence aug-cc-pVXZ basis sets, with empty symbols represening ANO-RCC basis set contracted to the size of the aug-cc-pVQZ basis. Right hand side: series of core-valence aug-cc-pCVXZ basis sets.

139x91mm (600 x 600 DPI)

139x94mm (600 x 600 DPI)