



**HAL**  
open science

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

Michal Kraus, Lucia Šimová, Pavel Neogrády, Miroslav Urban

### ► To cite this version:

Michal Kraus, Lucia Šimová, Pavel Neogrády, Miroslav Urban. Core - valence correlation effects in the ground and low - lying excited states of GaN. *Molecular Physics*, 2010, 108 (03-04), pp.467-476. 10.1080/00268970903563477 . hal-00580679

**HAL Id: hal-00580679**

**<https://hal.science/hal-00580679>**

Submitted on 29 Mar 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



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

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2009-0402.R1
Manuscript Type:	Special Issue Paper - In honour of Prof Werner 60th birthday
Date Submitted by the Author:	09-Dec-2009
Complete List of Authors:	Kraus, Michal; Faculty of natural Sciences, Comenius university, Department of physical and theoretical chemistry Šimová, Lucia; Faculty of natural Sciences, Comenius university, Department of physical and theoretical chemistry Neogrady, Pavel; Faculty of natural Sciences, Comenius university, Department of physical and theoretical chemistry Urban, Miroslav; Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Institute of Materials Science; Faculty of natural Sciences, Comenius university, Department of physical and theoretical chemistry
Keywords:	GaN molecular properties, excited states, core correlation effects, CCSD(T), CASPT2, aug-cc-pVXZ and aug-cc-PCVXZ basis sets
<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>GaN_final.tex</p>	

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



For Peer Review Only

## RESEARCH ARTICLE

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

Michal Kraus<sup>a</sup>, Lucia Šimová<sup>a</sup>, Pavel Neogrady<sup>a</sup> and Miroslav Urban<sup>a,b\*</sup>

<sup>a</sup>Department of physical and theoretical chemistry, Faculty of natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia; <sup>b</sup>Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Institute of Materials Science, J. Bottu 25, 917 24 Trnava, Slovakia.

(v4.5 released September 2009)

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  $3d^{10}4s^24p^1$  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 ( $X=T, Q,$

---

\* Corresponding author. Email: urban@fns.uniba.sk

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  $\text{Ga}_2$  up to  $\text{Kr}_2$  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

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

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

15 Along with results using the aug-cc-pVXZ ( $X=T, Q, 5$ ) and aug-cc-pCVXZ ba-  
16 sis sets we also present CCSD(T)-DKH calculations with the relativistically con-  
17 structed ANO-RCC (Atomic Natural Orbitals) basis set [16]. ANO-RCC basis sets  
18 for Ga and N were contracted to the size corresponding to the aug-cc-pVQZ basis.  
19 The difference is that the aug-cc-pVQZ basis was constructed with correlating  
20 only three valence electrons of Ga, whereas the ANO-RCC basis set was developed  
21 having in mind correlation of 13 outer shells  $3d^{10} 4s^2 4p^1$  electrons of the Ga atom.  
22  
23  
24  
25  
26  
27

## 28 2. Computational details

29 All calculations were carried out with the MOLCAS suite of programs [17]. The  
30 CCSD(T) Coupled Cluster method with single and double excitations and pertur-  
31 bative triples [18, 19] with an approximate spin adaptation [20] was employed in all  
32 calculations using the Restricted Hartree Fock reference for high spin open-shell  
33 states. Our method is similar to the approach developed independently by Knowles,  
34 Hampel and Werner [21]. This method leads to energies which are very close to  
35 the energies obtained by the rigorous (even if slightly more demanding) method  
36 [22] for the spin adaptation. Denominators in perturbatively calculated triples were  
37 diagonal Fock-matrix elements [23], see also Refs. [20, 24]. In all calculations we  
38 have considered scalar relativistic effects using the second-order spin-free scalar  
39 relativistic approach introduced by Douglas, Kroll, and Hess (DKH) [8].

40 The evaluation of the dipole moment and the parallel  $zz$  component of the dipole  
41 polarizability was accomplished using the numerical finite field perturbation ap-  
42 proach [25]. The strength of the external electric field was 0.001, 0.002, and 0.004  
43 au, respectively. Final dipole moments and dipole polarizabilities were obtained us-  
44 ing the numerical derivatives prescription, which allow to remove the higher order  
45 terms [26, 27].

46 Five correlation schemes were used for aug-cc-pVXZ, aug-cc-pCVXZ ( $X=T, Q, 5$ ),  
47 and ANO-RCC basis sets. For the gallium atom we correlated 3 valence ( $4s^2 4p^1$ )  
48 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.  
49 These four correlation schemes for Ga were combined with correlating five valence  
50 electrons of the nitrogen leading to the total number of 8, 18, 24, or 26 correlated  
51 electrons of the three states of GaN. In addition, the ( $3s^2 3p^6 3d^{10} 4s^2 4p^1$ ) correlation  
52 scheme of 21 electrons of Ga was combined with correlating all seven electrons of  
53 nitrogen, leading to the total number of 28 correlated electrons. Some data, not  
54 presented here, were also obtained by correlating all 31 electrons of Ga.  
55  
56  
57  
58

59 Basis sets used for calculations of molecular properties of GaN molecule differ in  
60

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-

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24

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.

25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44

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

45  
46  
47  
48  
49  
50  
51

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.

52  
53  
54  
55  
56  
57  
58  
59  
60

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



1 agree very well, to within 0.02 eV or even better for aug-cc-pVQZ, aug-cc-pCVQZ,  
 2 and ANO-RCC basis sets. Thus, somewhat surprisingly, there are no remarkable  
 3 differences in the performance of the three basis sets in CCSD(T) calculations of  
 4  $D_e$ . This holds for all three states considered in this work. Yet, there is an indication  
 5 signaling inferior performance of the aug-cc-pVQZ basis set. Good results with  
 6 this basis are accompanied by quite large BSSE (see last three columns of Table  
 7 3), 0.1 up to 0.4 eV for the three states. The only exception is  $D_e$  calculated with  
 8 8 correlated electrons. Large BSSE compensates the deficiency of the insufficient  
 9 description of the deeper electron shells of the Ga atom with the aug-cc-pVQZ  
 10 basis set. BSSE is small for ano-rcc basis when we correlate 3d electrons of gallium  
 11 (which is exactly what it was constructed for). In case of aug-cc-pCVQZ basis BSSE  
 12 is order of magnitude smaller than with the aug-cc-pVQZ basis for all correlation  
 13 schemes. Exaggerated importance of the BSSE correction when the basis set is not  
 14 appropriate for the number of electrons which are correlated was also observed in  
 15 calculations of  $D_e$  for the ground state of GaN and for  $\text{Ga}_2$  by Tzeli and Tsekouras  
 16 [2]. Their CCSD(T) CBS limit for  $D_e$  of the ground state (2.12 eV) obtained with 18  
 17 correlated electrons employing small-core relativistic pseudopotentials basis agrees  
 18 reasonably well with our best value, 2.140 eV (Table 5).  
 19

20  
 21 As mentioned above, the second excited  $a^1\Sigma^+$  state dissociates via the  $\text{Ga } ^2P +$   
 22  $\text{N } ^2D$  channel. Since the doublet state of the nitrogen atom shows a multireference  
 23 character which is accompanied by high excitation amplitudes (up to 0.28) in the  
 24 single reference CCSD calculation, results with the single-determinant reference  
 25 CCSD(T) method may not be conclusive due to quasidegeneracy effects. To ensure  
 26 that our conclusions concerning the performance of differently constructed basis  
 27 sets are not plagued by quasidegeneracy effects, we used the CASPT2 method  
 28 for evaluation of dissociation energies of all three electronic states along with  
 29 CCSD(T). The active space contains 8 valence electrons in 8 active orbitals (4s4p  
 30 of the gallium atom and 2s2p orbitals of the nitrogen atom). CASPT2 dissociation  
 31 energies with 26 correlated electrons using aug-cc-pVQZ, aug-cc-pCVQZ  
 32 and ANO-RCC basis sets are presented in Table 3. Comparison of CCSD(T) and  
 33 CASPT2 dissociation energies with the series of aug-cc-pCVXZ basis sets (X=T,  
 34 Q, and 5) is shown in Table 5 for 28 correlated electrons. For the ground  $X^3\Sigma^-$  state  
 35 CCSD(T) and CASPT2 results differ **by less than** 0.1 eV, CASPT2  $D_{e,s}$  values  
 36 being slightly higher than CCSD(T) dissociation energies. Similarly, CASPT2 disso-  
 37 ciation energies of the first  $A^3\Pi$  excited state are higher than CCSD(T) ones, this  
 38 time by 0.12 to 0.17 eV. Conversely, for the  $a^1\Sigma^+$  state is the CASPT2 dissociation  
 39 energy lower than the CCSD(T) energy. This reflects the overestimated energy of  
 40 the nitrogen  $^2D$  state by CCSD(T). The importance of triples in CCSD(T) can be  
 41 determined by comparing CCSD(T) and CCSD dissociation energies in Table 5.  
 42 For the ground state this contribution is relatively small, 0.1 eV, but for the  $A^3\Pi$   
 43 and the  $a^1\Sigma^+$  states it increases up to 0.2 and almost 0.5 eV, respectively. There-  
 44 fore, comparisons of CCSD(T), CCSD, and CASPT2 data demonstrate that details  
 45 of the treatment of correlation effects matter. Concerning BSSE, conclusions from  
 46 CASPT2 and CCSD(T) data for  $D_e$  are completely the same: BSSE is much larger  
 47 for aug-cc-pVQZ basis set than for the aug-cc-pCVQZ basis. With CASPT2 it is  
 48 larger than with CCSD(T) with all three bases.  
 49  
 50  
 51  
 52  
 53  
 54

### 55 3.3. DIPOLE MOMENTS AND DIPOLE POLARIZABILITIES

56 The performance of aug-cc-pVQZ, aug-cc-pCVQZ and ANO-RCC basis sets in  
 57 calculations of dipole moments and parallel dipole polarizabilities with 8 to 28  
 58 correlated electrons is documented in Table 4. Optimized internuclear distances  
 59  
 60

1 are taken from Tables 1 and 2 for each particular correlation scheme and the  
2 basis set. Originally, we expected that dipole moments and polarizabilities will be  
3 very sensitive to the number of correlated electrons and the basis set. It appears,  
4 however, that the sensitivity of electric properties to the basis set is not dramatic.  
5 For example, considering 26 correlated electrons for the ground state with the aug-  
6 cc-pVQZ basis set (inappropriate basis for this calculation) the dipole moment is  
7 0.719 a.u. It differs by 9.1 % from the aug-cc-pCVQZ basis set result. Note that  
8 ANO-RCC result differs from this reference number much less, by 3.3 %. The  
9 basis set dependence for both dipole moment and polarizability with the aug-cc-  
10 pCVXZ series and 28 correlated electrons is even smaller, as expected, see Table 5.  
11 Aside from data obtained with 8 correlated electrons, dipole moments and dipole  
12 polarizabilities are insensitive also to the number of correlated electrons. With all  
13 basis sets the CCSD(T) dipole moments of GaN with 18-26 correlated electrons lie  
14 in the interval narrower than 0.02 a.u. for all states. Core correlation effect due to  
15 correlating inner shell 1s electrons of nitrogen is 0.005 a.u. for the  $a^1\Sigma^+$  state and  
16 even smaller for the ground and the  $A^3\Pi$  excited states. Analogous insensibility  
17 holds for the parallel polarizability.  
18  
19  
20  
21  
22

### 23 3.4. EXCITATION ENERGIES

24 Adiabatic CCSD(T)-DKH excitation energies  $T_e$  from the ground  $X^3\Sigma^-$  state to  
25 the first two excited  $A^3\Pi$  and  $a^1\Sigma^+$  states, respectively, are much more sensitive  
26 to the selection of the basis set and proper correlation scheme than are other  
27 properties. Nevertheless, when discussing details of the basis set effects we should  
28 realize that the energy gap between the ground  $X^3\Sigma^-$  state and the  $A^3\Pi$  excited  
29 state is quite small.  
30

31 For the two states with 8-28 correlated electrons **the basis set dependence**  
32 **of  $T_e$  is transparently** demonstrated in Figures 1 and 2, respectively. On the  
33 left hand side we present the series aug-cc-pVXZ (X= T, Q, and 5), supplemented  
34 with ANO-RCC results. On the right hand side there are excitation energies with  
35 the aug-cc-pCVXZ series. For both series we also present CBS limits. Not much  
36 discussion is needed for results with 8 correlated electrons. Excitation energies  
37 with all basis sets are quite similar, the basis set dependence for both aug-cc-  
38 pVXZ and aug-cc-pCVXZ series is smooth, but excitation energies are much too  
39 high. More interesting are results with 18-28 electrons. As a curiosity we note that  
40  $T_e$  with the smallest aug-cc-pVTZ basis and 18 correlated electrons agrees very  
41 well with the CBS limit calculated from much more demanding aug-cc-pCVXZ  
42 series, 0.104 and 0.747 eV for  $A^3\Pi$  and  $a^1\Sigma^+$  states, respectively. Typically, this  
43 is a good result for the wrong reason. Upon correlating 26 or 28 electrons and  
44 extending the aug-cc-pVTZ basis to aug-cc-pVQZ the excitation energy of the  
45  $A^3\Pi$  state diminishes to about 0.04 eV. Extrapolating to the CBS limit with these  
46 two basis sets we would obtain completely misleading result, 0.007 eV with 28  
47 correlated electrons. This may lead to some doubts about the state ordering in  
48 GaN. We remind that there was a long lasting discussion about the ordering of  
49 states for valence isoelectronic BN and AlN molecules stressing the importance of  
50 proper handling of electron correlation effects for these species [29, 30]. When  
51 calculating the CBS limit using smaller aug-cc-pVXZ series one should be careful  
52 since the behavior of  $T_e$  with respect to the cardinal number X is oscillatory for  
53 both excited states. In any case, the smallest aug-cc-pVTZ must be avoided in  
54 the extrapolation to the CBS limit **when core electrons are correlated**. In  
55 contrast,  $T_e$  is much less sensitive to the cardinal number in the aug-cc-pCVXZ  
56 series, it is also almost insensitive to the number of correlated electrons, the basis  
57  
58  
59  
60

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  $829\text{ cm}^{-1}$ . 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,  $532\text{ cm}^{-1}$  in comparison with CCSD(T) ( $857\text{ cm}^{-1}$ ). 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**

1 performance of aug-cc-pVXZ and aug-cc-pCVXZ basis sets (with X go-  
2 ing up to quintuple zeta for both series in the present study) in accurate  
3 calculations of these properties of the GaN ground  $X^3\Sigma^-$  state are the  
4 same. These result are supplemented in this paper by correlating deeper  
5 shells of GaN and its low-lying excited states. It appears that excitation  
6 energies are most sensitive to proper selection of the basis set as used  
7 with different correlation schemes. Our excitation energy for the  $A^3\Pi$  state  
8 agrees reasonably well with the value published by Denis and Balasubramanian [4],  
9 0.106 eV. However, their value for the  $a^1\Sigma^+$  state is overestimated in comparison  
10 with our CBS limit (Table 5) by 0.05 eV. This state is more sensitive to basis  
11 set effects. Concerning electric properties, we were only able to compare electric  
12 dipole moments from the work of Denis and Balasubramanian, obtained by the  
13 multireference MRSDCI method finding the differences from our results of about  
14 0.1 a.u. for the three states.  
15

16  
17 Our systematic investigation of the accuracy, reliability and efficiency for calcula-  
18 tions of molecular properties of GaN as a typical species containing a IIIA element  
19 leads us to several conclusions on the use of differently constructed basis sets for  
20 the treatment of the core-correlation effects. Clearly, it would be advantageous  
21 to use relatively smaller aug-cc-pVXZ basis sets for considering the core-valence  
22 correlation effects. These basis sets are usually flexible enough in many applica-  
23 tions and are smaller than their aug-cc-pCVXZ counterparts. Clearly, some data  
24 obtained with these basis sets agree with the CBS limit quite well. However, we  
25 were unable to obtain good results in a systematic and controlled manner. Simply,  
26 these basis sets were not constructed for core-valence correlations. Yet, consider-  
27 ing at least  $3d$  electrons for such species is inevitable. In light of this fact and  
28 the unreliable performance of the valence aug-cc-pVXZ basis sets when correlating  
29 deeper shels of Ga we see little space for using these basis sets as a predictive  
30 tool for properties of molecules containing these atoms. Main obstacle is our find-  
31 ing that molecular properties calculated with aug-cc-pVXZ basis sets suffer from  
32 the oscillatory behavior with increasing cardinal number. Smaller members of the  
33 series, as the aug-cc-pVTZ basis set, should be avoided in any extrapolations to  
34 the CBS limit **when core electrons are correlated**. Then the advantage of its  
35 relatively smaller size is lost. For larger-scale calculations of IIIA elements com-  
36 pounds we would prefer smaller members of the aug-cc-pCVXZ series. A typical  
37 example is the aug-cc-pCVQZ basis set (279 basis functions) which mostly outper-  
38 forms the aug-cc-pV5Z basis with 267 basis functions. Large number of virtuals  
39 can be circumvented by using the truncated space obtained by the OVOS (Opti-  
40 mized Virtual Orbital Space) technique [34]. Utilizing the fact that for virtually all  
41 properties calculated in this paper the effect of core valence electrons beyond  $3d$   
42 was relatively small we can restrict ourselves just to these electrons. For a single  
43 basis set calculation very good compromise between the accuracy and efficiency  
44 offer the ANO-RCC basis sets.  
45  
46  
47  
48  
49

#### 50 4. Acknowledgements

51  
52 This work was supported by the Slovak Research and Development Agency, con-  
53 tracts No. APVV-20-018405, APVV-LPP-0155-09, and the Slovak Grant Agency  
54 VEGA under the contract No. 1/0428/09. Support from EURATOM, contract  
55 No.FU07-CT-2006-00441 is also gratefully acknowledged.  
56  
57  
58  
59  
60

## References

- [1] N.J. DeYonker, K.A. Peterson and A.K. Wilson, *J. Phys. Chem. A* **111**, 11383 (2007).
- [2] D. Tzeli and A.A. Tsekouras, *J. Chem. Phys.* **128**, 144103 (2008).
- [3] Y. Mochizuki and K. Tanaka, *Theor. Chem. Acc.* **101**, 292 (1999).
- [4] P.A. Denis and K. Balasubramanian, *Chem. Phys. Lett.* **423**, 247 (2006).
- [5] L. Šimová, D. Tzeli, M. Urban, I. Černušák, G. Theodorakopoulos and I.D. Petsalakis, *Chem. Phys.* **349**, 98 (2008).
- [6] A.K. Wilson, D.E. Woon, K.A. Peterson and T.H. Dunning Jr., *J. Chem. Phys.* **110**, 7667 (1999).
- [7] S.F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- [8] G. Jansen and B.A. Hess, *Phys. Rev. A* **39**, 6016 (1989).
- [9] M. Zhou and L. Andrews, *J. Phys. Chem. A* **104**, 1648 (2000).
- [10] J. Zhao, B. Wang, X. Zhou, X. Chen and W. Lu, *Chem. Phys. Lett.* **422**, 170 (2006).
- [11] A. Costales and R. Pandey, *J. Chem. Phys. A* **107**, 191 (2003).
- [12] A.K. Kandalam, R. Pandey, M.A. Blanco, A. Costales, J.M. Recio and J.M. Newsam, *J. Phys. Chem. B* **104**, 4361 (2000).
- [13] D. Tzeli, I.D. Petsalakis and G. Theodorakopoulos, *Chem. Phys. Lett.* **448**, 88 (2007).
- [14] H. Suzuki, R. Togashi, H. Murakami, Y. Kumagai and A. Koukitu, *J. Crystal Growth* **310**, 1632 (2008).
- [15] L.T. Ueno, O. Roberto-Neto, S. Canuto and F.B.C. Machado, *Chem. Phys. Lett.* **413**, 65 (2005).
- [16] B.O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, *J. Phys. Chem. A* **108**, 2851 (2004).
- [17] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-Å. Malmqvist, P. Neogrady, T. B. Pedersen, M. Pitoňák, M. Reiher, B.O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov and R. Lindh, *J. Comput. Chem.* **31**, 224 (2010).
- [18] G. Karlström, R. Lindh, P.-Å. Malmqvist, B.O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady and L. Seijo, *Computational Materials Science* **28**, 222 (2003).
- [19] M. Urban, J. Noga, S.J. Cole and R.J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985).
- [20] K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- [21] M. Urban, P. Neogrady, and I. Hubač, in *Recent Advances in Coupled-Cluster Methods*, edited by Rodney J. Bartlett (World Scientific, Singapore, 1997), pp. 275 - 306.
- [22] P.J. Knowles, C. Hampel and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).
- [23] M. Heckert, O. Heun, J. Gauss and P.G. Szalay, *J. Chem. Phys.* **124**, 124105 (2006).
- [24] P. Neogrady and M. Urban, *Int. J. Quantum Chem.* **55**, 187 (1995).
- [25] J.D. Watts, J. Gauss and R.J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- [26] I. Černušák, G.H.F. Dierksen and A.J. Sadlej, *Phys. Rev. A* **33**, 814 (1986).
- [27] G. Maroulis, *J. Chem. Phys.* **108**, 5432 (1998).
- [28] D. Jacquemin, B. Champagne and J.M. André, *Int. J. Quantum Chem.* **65**, 679 (1997).
- [29] T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- [30] X. Li and J. Paldus, *Chem. Phys. Lett.* **431**, 179 (2006).
- [31] G.L. Gutsev, P. Jena, and R.J. Bartlett, *J. Chem. Phys.* **110**, 2928 (1999).
- [32] L. Demović, I. Černušák, G. Theodorakopoulos, I.D. Petsalakis, and M. Urban, *Chem. Phys. Lett.* **447**, 215 (2007).
- [33] B. Manna, K.K. Das, *J. Mol. Struct. - Theochem* **467**, 135 (1995).
- [34] T. Shirai, J. Reader, A.E. Kramida and J. Sugar, *J. Phys. Chem. Ref. Data* **36**, 509 (2007).
- [35] P. Neogrady, M. Pitoňák, and M. Urban, *Mol. Phys.* **103** 2141 (2005).

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			aug-cc-pV5Z 267	Extrapolation	
		ano-rcc <sup>a</sup> 173	aug-cc-pVTZ 105	aug-cc-pVQZ 173		(T,Q,5)	(Q,5)
$X - ^3\Sigma^-$	8	3.858	3.874	3.863	3.860	3.856	<b>3.857</b>
	18	<b>3.757</b>	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	<b>3.614</b>
	18	<b>3.485</b>	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	<b>3.323</b>
	18	<b>3.206</b>	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

<sup>a</sup> - 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	<b>3.750</b>
$A - ^3\Pi$	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	<b>3.480</b>
$a - ^1\Sigma^+$	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	<b>3.199</b>

## REFERENCES

13

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 <sup>a</sup>	aug-cc-pVQZ	aug-cc-pCVQZ	ano-rcc <sup>a</sup>
X - $^3\Sigma^-$	8	<b>1.999</b>	2.009	2.002	<b>0.007</b>	0.005	0.007
	18	2.062	2.071	<b>2.065</b>	0.133	0.015	<b>0.045</b>
	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	<b>2.065</b>	2.059	0.230	<b>0.019</b>	0.217
A - $^3\Pi$	8	<b>1.824</b>	1.832	1.827	<b>0.008</b>	0.006	0.008
	18	1.949	1.959	<b>1.956</b>	0.173	0.018	<b>0.051</b>
	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	<b>1.949</b>	1.948	0.305	<b>0.023</b>	0.244
a - $^1\Sigma^+$	8	<b>3.733</b>	3.750	3.751	<b>0.010</b>	0.008	0.010
	18	3.960	3.966	<b>3.972</b>	0.221	0.024	<b>0.060</b>
	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	<b>3.970</b>	3.974	0.397	<b>0.030</b>	0.276

<sup>a</sup> - basis set was contracted to size aug-cc-pVQZ basis set.

<sup>b</sup> - dissociation products were  $^2P$  Ga and  $^4S$  N.

<sup>c</sup> - 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 <sup>a</sup>	aug-cc-pVQZ	aug-cc-pCVQZ	ano-rcc <sup>a</sup>
X - $^3\Sigma^-$	8	<b>0.823</b>	0.821	0.812	<b>56.85</b>	56.69	55.34
	18	0.735	0.780	<b>0.767</b>	53.45	53.98	<b>52.62</b>
	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	<b>0.793</b>	0.759	52.74	<b>53.97</b>	52.11
A - $^3\Pi$	8	<b>1.131</b>	1.127	1.117	<b>60.56</b>	60.53	59.53
	18	1.061	1.075	<b>1.063</b>	58.13	57.53	<b>56.52</b>
	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	<b>1.081</b>	1.059	57.91	<b>57.30</b>	56.26
a - $^1\Sigma^+$	8	<b>1.662</b>	1.670	1.659	<b>59.69</b>	59.61	58.31
	18	1.538	1.542	<b>1.531</b>	54.03	54.01	<b>52.95</b>
	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	<b>1.551</b>	1.534	53.77	<b>53.97</b>	52.76

<sup>a</sup> - basis set was contracted to size aug-cc-pVQZ basis set.

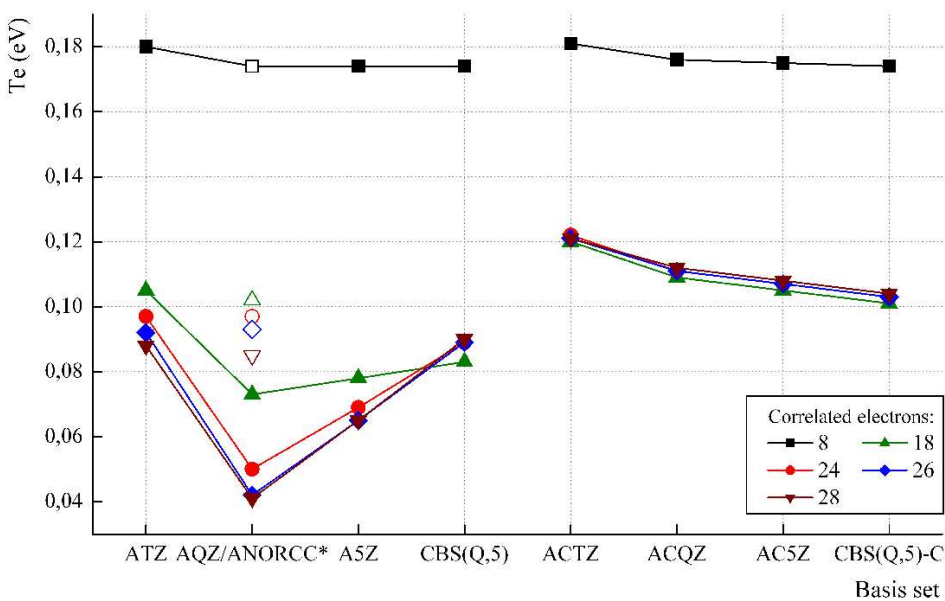
Table 5. Excitation energies (eV), BSSE corrected dissociation energies<sup>a</sup> (eV), dipole moments (a.u.) and polarizabilities (a.u.) of first tree states of the GaN molecule obtained at CCSD(T) DKH level using aug-cc-pCVXZ (X=T,Q,5) basis sets and correlating 28 electrons. Two extrapolation schemes 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)	<b>2.140(2.254)</b>
	$D_e(CCSD)$	1.836	1.933	1.966		
	$\mu_z$	0.773	0.780	0.781	0.784	<b>0.782</b>
	$\alpha_{zz}$	54.23	53.63	53.42	53.20	<b>53.20</b>
	$\alpha_{xx}$	50.72 <sup>b</sup>	49.74 <sup>b</sup>			
$A^{-3}\Pi$	$T_e$	0.122(0.063)	0.112(0.038)	0.108(0.030)	0.104	<b>0.104</b>
	$T_e(CCSD)$	0.221	0.214	0.212		
	$D_e$	1.827(1.934)	1.949(2.103)	1.991(2.155)	2.037(2.219)	<b>2.035(2.210)</b>
	$D_e(CCSD)$	1.606	1.715	1.753		
	$\mu_z$	1.065	1.074 <sup>b</sup>	1.076 <sup>b</sup>	1.080	<b>1.078</b>
	$\alpha_{zz}$	57.48	57.24 <sup>b</sup>	57.06 <sup>b</sup>	56.98	<b>56.87</b>
$a^{-1}\Sigma^{+}$	$T_e$	0.829(0.752)	0.780(0.702)	0.764(0.686)	0.746	<b>0.747</b>
	$T_e(CCSD)$	1.308	1.274	1.262		
	$D_e$	3.833(3.550)	3.969(3.793)	4.015(3.835)	4.066(3.931)	<b>4.063(3.879)</b>
	$D_e(CCSD)$	3.391	3.502	3.539		
	$\mu_z$	1.542	1.547	1.548	1.550	<b>1.549</b>
	$\alpha_{zz}$	54.16	53.81	53.63	53.51	<b>53.44</b>

<sup>a</sup> - spin-orbit correction for Ga <sup>2</sup>P is 0.068 eV.

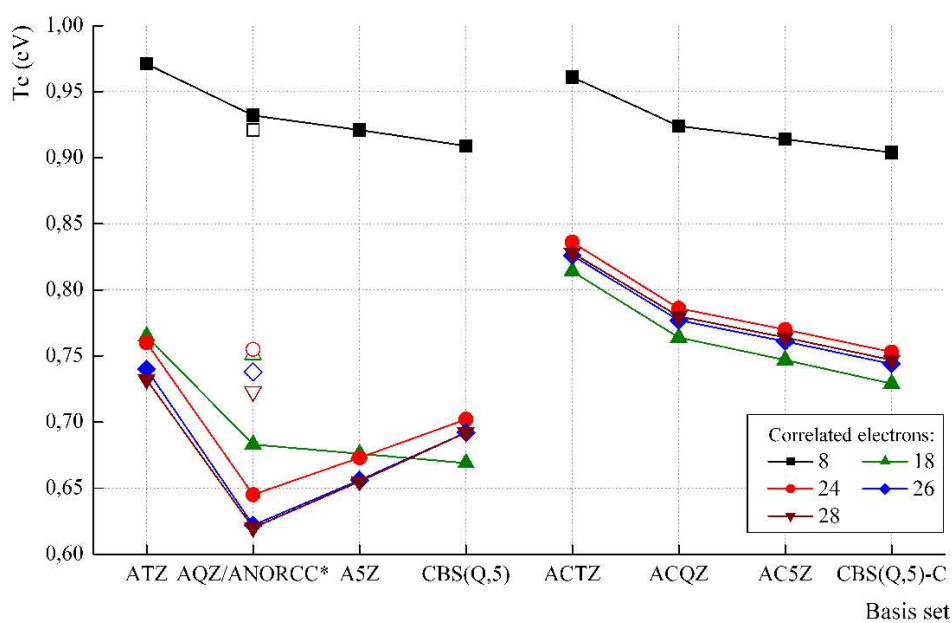
<sup>b</sup> - used field strength 0.002 0.004 and 0.008.

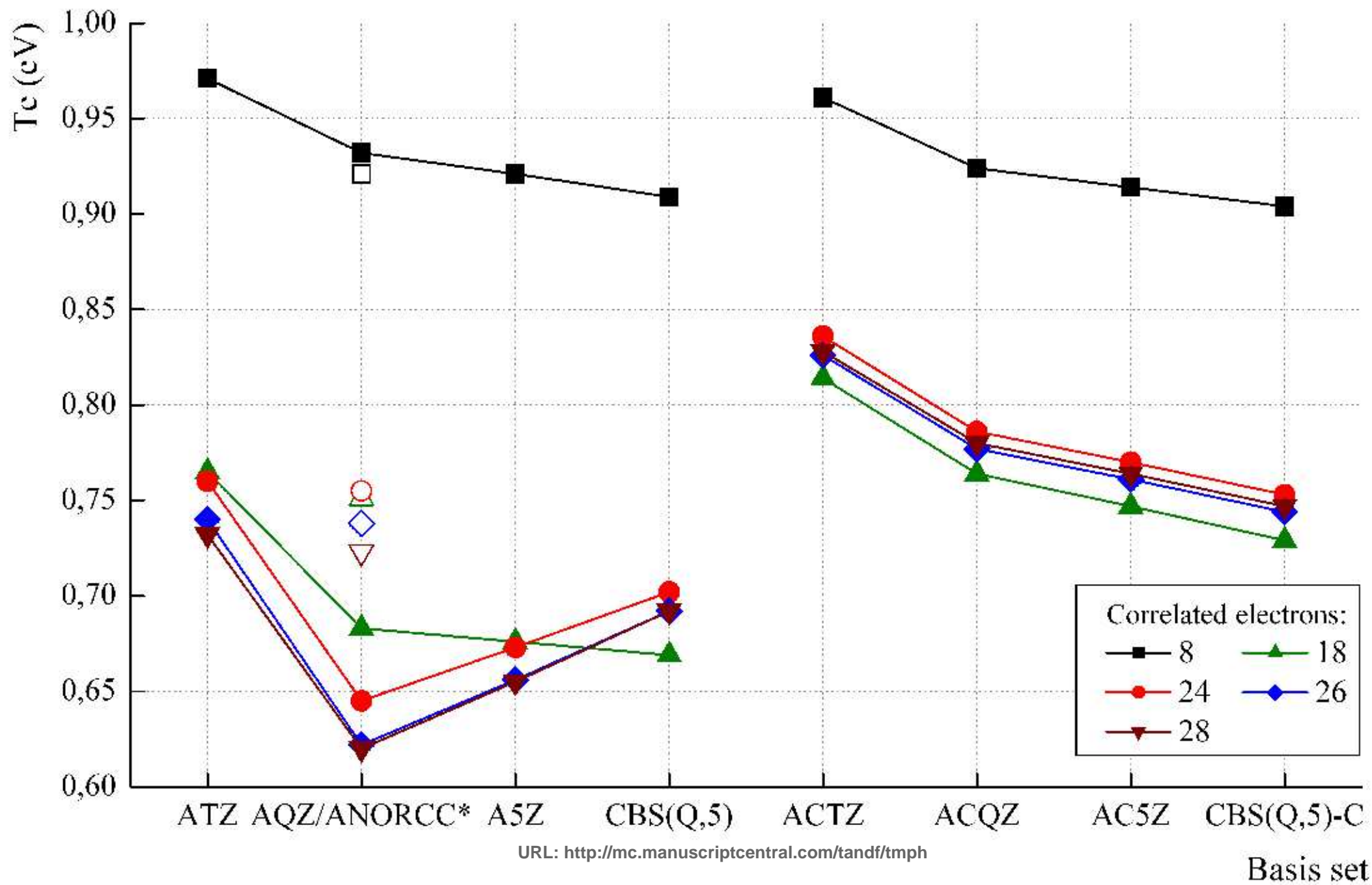
Figure 1. CCSD(T) DKH excitation energies for GaN A <sup>3</sup>Π state. The left hand side: Series of valence aug-cc-pVXZ basis sets, with empty symbols representing ANO-RCC basis set contracted to the size of the aug-cc-pVQZ basis. Right hand side: series of core-valence aug-cc-pCVXZ basis sets.

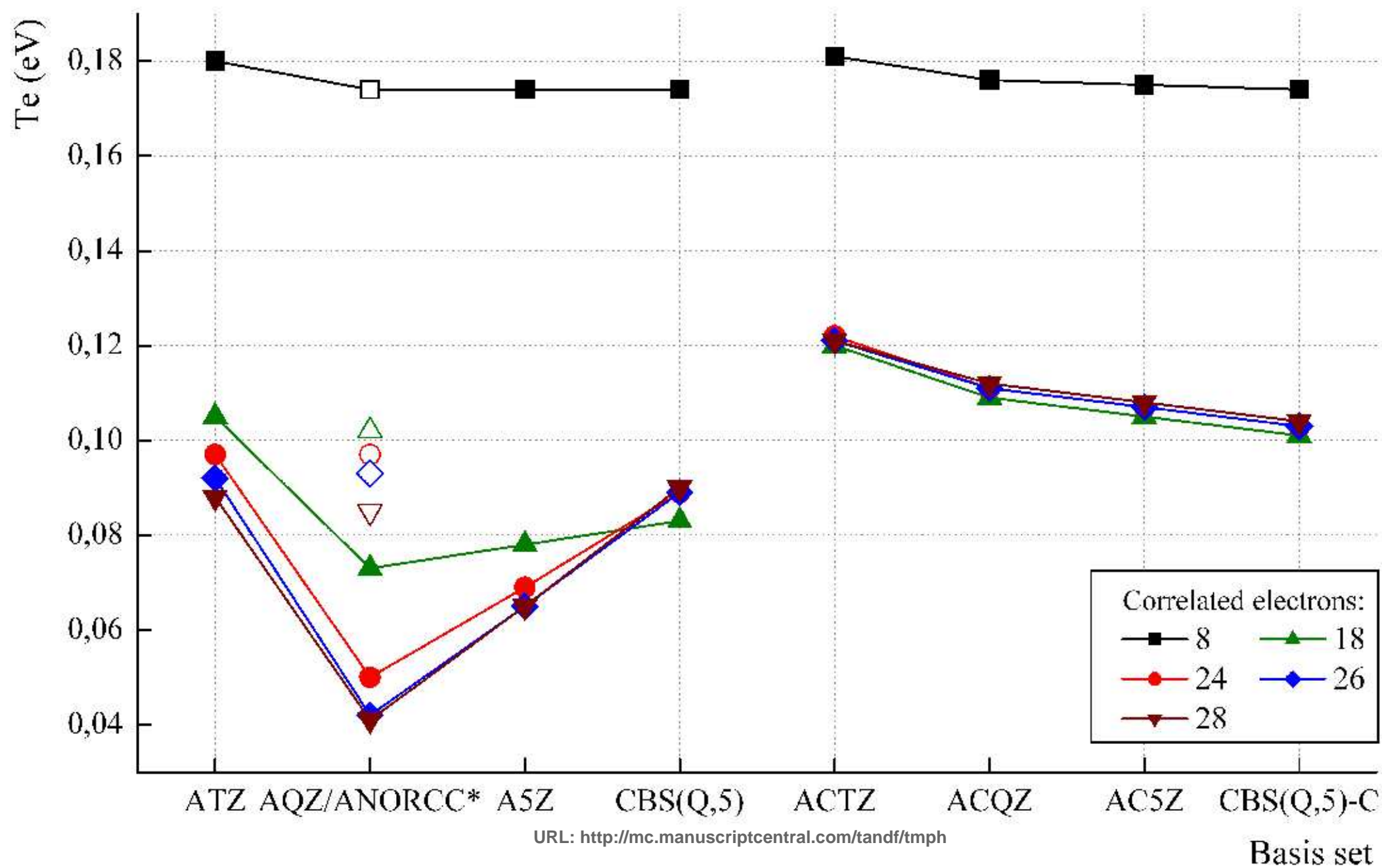


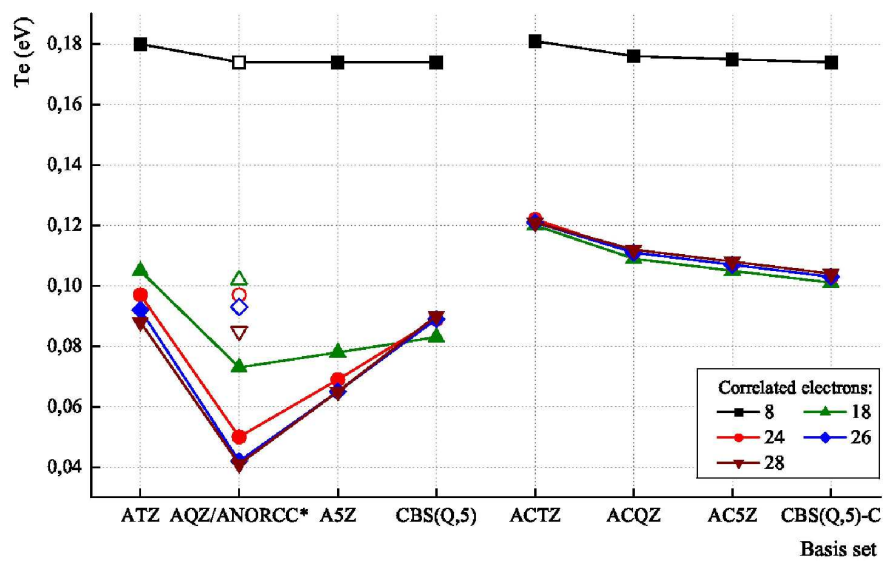
Peer Review Only

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 representing 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.

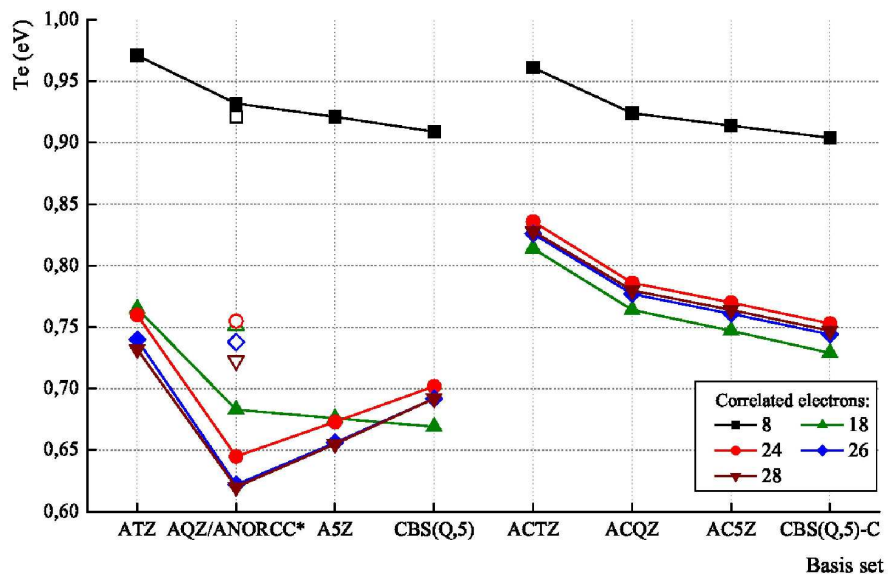








139x91mm (600 x 600 DPI)



139x94mm (600 x 600 DPI)