

The electron affinity of gallium nitride (GaN) and digallium nitride (GaNGa): The importance of the basis set superposition error in strongly bound systems

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The electron affinity of GaN and Ga₂N as well as the geometries and the dissociation energies of the ground states of gallium nitrides GaN, GaN⁻, Ga₂N, and Ga₂N⁻ were systematically studied by employing the coupled cluster method, RCCSD(T), in conjunction with a series of basis sets, (aug-)cc-pVxZ(-PP), x=D, T, Q, and 5 and cc-pwCVxZ(-PP), x=D, T, and Q. The calculated dissociation energy and the electron affinity of GaN are 2.12 and 1.84 eV, respectively, and those of Ga₂N are 6.31 and 2.53 eV. The last value is in excellent agreement with a recent experimental value for the electron affinity of Ga₂N of 2.506 ± 0.008 eV. For such quality in the results to be achieved, the Ga 3*d* electrons had to be included in the correlation space. Moreover, when a basis set is used, which has not been developed for the number of the electrons which are correlated in a calculation, the quantities calculated need to be corrected for the basis set superposition error.

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I. INTRODUCTION

Among semiconductor materials, gallium nitride (GaN) has received considerable attention lately because of its current and possible future applications. In an attempt to understand the fundamental properties of solid, several papers have concentrated on the properties of small fragments such as dimers (GaN),¹⁻⁴ trimers [GaN₂ (Refs. 2 and 5-7) and Ga₂N (Refs. 5 and 8)], etc., either neutral or charged, both experimentally and theoretically. Recently, Sheehan *et al.*⁸ looked at the electron affinity (EA) of the linear GaNGa molecule. Using photoelectron spectroscopy, they determined an experimental value of 2.506 ± 0.008 eV. Previous theoretical studies found the EA ranging from 1.52 [complete active space self-consistent field (CASSCF)]⁵ to 2.36 eV (B3LYP/aug-cc-pVDZ).⁸ For GaN, there is only a theoretically estimated EA of 1.44 ± 0.5 eV by Denis and Balasubramanian.⁴

Since these theoretical values have a large error bar and the accurate calculation of the EA is a challenge, we tried to perform a systematic study on the ground states of gallium nitrides GaN, GaN⁻, Ga₂N, and Ga₂N⁻ in order to determine an exact value for the EAs as well as for the geometries and the dissociation energies employing the coupled cluster method, RCCSD(T), in conjunction with a series of basis sets. Moreover, aiming at an accurate determination of the above quantities, the basis set superposition error (BSSE) must be taken into account. In the literature, the correction of the BSSE has been studied for various diatomic, triatomic, or polyatomic systems.⁹ Furthermore, the effect of the BSSE

correction of the potential energy curves surfaces has also been studied for some systems, for example, for some hydrogen-bonded dimers¹⁰ or for the GaN₂⁺ cation.⁶

II. METHODOLOGY

For N atom, the correlation consistent basis sets of Dunning¹¹ cc-pVxZ and aug-cc-pVxZ, x=D, T, Q, and 5 were used; the basis sets range in size from (9*s*4*p*1*d*) → [3*s*2*p*1*d*] to (15*s*9*p*5*d*4*f*3*g*2*h*) → [7*s*6*p*5*d*4*f*3*g*2*h*]. For Ga atom, Peterson's¹² correlation consistent-like basis sets were chosen, which employ accurate small-core (1*s*²2*s*²2*p*⁶, i.e., ten electrons) relativistic pseudopotentials, i.e., cc-pVxZ-PP(vxz), aug-cc-pVxZ-PP(avxz), x=D, T, Q, and 5. These basis sets treat the 3*s*²3*p*⁶3*d*¹⁰4*s*²4*p*¹ electrons in the *ab initio* calculation, were developed only for 4*s*4*p* correlation, and range in size from (8*s*7*p*7*d*) → [4*s*3*p*2*d*] to (17*s*14*p*14*d*4*f*3*g*2*h*) → [8*s*7*p*6*d*4*f*3*g*2*h*]. Additional calculations were performed with Peterson's¹³ correlation consistent-like weighted core basis sets, which employ also accurate small-core (1*s*²2*s*²2*p*⁶) relativistic pseudopotentials, i.e., cc-pwCVxZ-PP(wcvxz), x=D, T, and Q. The latter treat the 3*s*²3*p*⁶3*d*¹⁰4*s*²4*p*¹ electrons in the *ab initio* calculation, were developed for 3*d*4*s*4*p* correlation, and range in size from (9*s*8*p*8*d*1*f*) → [5*s*4*p*3*d*1*f*] to (17*s*14*p*15*d*5*f*3*g*1*h*) → [8*s*7*p*7*d*5*f*3*g*1*h*].

In all RCCSD(T) calculations, the 2*s*²2*p*³ electrons of the N atom and the 4*s*²4*p*¹ or the 3*d*¹⁰4*s*²2*p*¹ electrons of the Ga atom were correlated. Moreover, using the counterpoise procedure, the BSSE (Refs. 14 and 10) was taken into account, even though these are strongly bound systems where BSSE is often thought to be insignificant. Both the geom-

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tries and the dissociation energies were BSSE corrected, i.e., geometric optimization with respect to the BSSE corrected energy.

In order to evaluate our RCCSD(T), which is a single-reference method, we checked the single (t_1) and the double (t_2) amplitudes and the T_1 diagnostic because large amplitudes¹⁵ and the T_1 diagnostic¹⁶ can usually be thought as an indicator of a multireference system. In all calculations, the t_1 and t_2 amplitudes were very small. In most cases, they were less than 0.05. Only in a few calculations on Ga_2N , t_1 was about 0.1 and in a few calculations on GaN and GaN^- , t_1 was about 0.2. Moreover, the T_1 diagnostic is about 0.02 or less in most calculations with the exception of the calculations of Ga_2N using the (aug)-cc-pVnZ(-PP) basis sets and correlating the $4s^2 4p^1$ electrons of Ga (Table I) where T_1 is about 0.04. Furthermore, the T_1 of the calculations of the GaN^- anion are about 0.07 using the (aug)-cc-pVnZ(-PP) basis sets correlating the $4s^2 4p^1$ electrons of Ga (Table I) and about 0.05 using the (aug)-cc-p(wC)VnZ(-PP) basis sets correlating the $3d^{10} 4s^2 4p^1$ electrons of Ga (Table II).

Complete basis set (CBS) limit values were estimated using the formula¹⁷ $y = y_{\text{CBS}} + B e^{-Cx}$, where x is the cardinal basis set number ($x=2, 3, 4$, and 5) and B and C are fitting constants.

All calculations were carried out with the MOLPRO suite of codes.¹⁸

III. RESULTS AND DISCUSSION

The ground states of the $\text{Ga}_2\text{N}(\tilde{X}^2\Sigma_u^+)$, $\text{Ga}_2\text{N}^-(\tilde{X}^1\Sigma_g^+)$, $\text{GaN}(X^3\Sigma^-)$, and $\text{GaN}^-(X^2\Sigma^+)$ species were optimized for three kinds of basis sets, cc-pVxZ_N/cc-pVxZ-PP_{Ga}, $x=2-5$ (vxz), aug-cc-pVxZ_N/aug-cc-pVxZ-PP_{Ga}, $x=2-5$ (avxz), and cc-pVxZ_N/cc-pwCVxZ-PP_{Ga}, $x=2-4$ (wcvxz) correlating the $(2s^2 2p^3)_\text{N}$ and $(4s^2 4p^1)_\text{Ga}$ electrons [small valence space (s calculations)] or correlating the $(2s^2 2p^3)_\text{N}$ and $(3d^{10} 4s^2 4p^1)_\text{Ga}$ electrons [large valence space (l calculations)]. The Ga–N bond length R , the dissociation energy D_e , and the adiabatic electron affinity EA of the ground states of the four molecules of the s calculations are given in Table I and those of the l calculations are given in Table II. The CBS limit of all calculated values for each kind of basis set is also given. Additionally, the BSSE corrected quantities are also computed. The adiabatic EA_{BSSE} is the difference of the minima (at R_{BSSE}) of the BSSE corrected absolute energy of anion and molecule. The R , D_e , and EA with respect to the basis set size of the Ga_2N and GaN molecules are plotted in Figs. 1–6.

Geometries. Our best value for the Ga_2N molecule is 1.767 Å [CBS limit of both wcvxz_1 and wcvxz_1(BSSE) calculations] (see Table II). In Fig. 1 and Table II, it is shown clearly that the R values of vxz_1 and avxz_1, where the number of correlated electrons is higher than that for which the basis set is developed, do not converge. Moreover, the R values for $x=4$ and 5 are shorter than our best result of 1.767 Å and in the augmented basis set are shorter by 0.01 Å. However, the BSSE corrected R values, R_{BSSE} , of the l calculations of both vxz and avxz converge very well to the same CBS limit, which is only 0.003 Å longer than

$R=1.767$ Å. This shows that the inclusion of the BSSE correction is necessary when the basis set is not developed for the number of correlated electrons.

Furthermore, the R and the R_{BSSE} values for both vxz_s and avxz_s calculations, where the basis sets are developed and used for $4s4p$ correlation only (which is what s calculations do), converge to the same CBS limit which is elongated by 0.06 Å compared to our best R value (see Tables I and II). This fact shows clearly that the inclusion of the correlation of the $3d$ electrons is necessary. Note that the differences between the R and R_{BSSE} values for vxz_s, avxz_s, and wcvxz_l calculations are one order of magnitude smaller compared to those for vxz_l and avxz_l. This shows that the BSSE becomes large when the basis set is not appropriate for the number of the correlating electrons but is not affected by the size of that number.

Wang and Balasubramanian⁵ present R values of 1.725 (MP2), 1.736 (CCD), 1.767 (CASSCF), and 1.778 Å (B3LYP) using a medium core relativistic effective core potential (RECP) for Ga and N, a double zeta quality basis set for the $3d4s4p$ electrons of Ga and $2s2p$ electrons of N and keeping the $3d$ electrons inactive. Sheehan *et al.*⁸ give $R=1.784$ Å (B3LYP/aug-cc-pVDZ). Our best value for the Ga_2N molecule is 1.767 Å [CBS limit of both wcvxz_1 and wcvxz_1(BSSE) calculations].

For the Ga_2N^- anion, our best CBS limit for the R value is 1.781 Å, 0.014 Å larger than the corresponding value of the neutral molecule. There is a slight difference in the CBS limit of the R and R_{BSSE} values in the wcvxz_l calculations which could be less if the corresponding quintuple zeta basis set were available. Previous studies^{5,8} gave R ranging from 1.749 (CCD)⁵ to 1.797 Å (B3LYP).⁸ Tables I and II show clearly that, as in the case of the neutral Ga_2N , the inclusion of the $3d$ electrons in the correlation is necessary, otherwise, there is an overestimation of the R distance by 0.06 Å. Moreover, they show that when the basis sets are used for more correlated electrons than the number of electrons for which they have been developed, an underestimation of the R distance in large basis sets ($x=4$ and 5) by 0.01 Å occurs and the curves with respect to the basis set size do not converge. However, the BSSE correction improves these R values and the resulting CBS limit is only overestimated by 0.003 Å.

For the GaN and GaN^- species, our best results of the R distances are the CBS limits of the wcvxz_1(BSSE) calculations, cf., 1.985 and 1.748 Å, respectively (see Table II and Fig. 2). The corresponding values of the vxz_1(BSSE) and avxz_1(BSSE) calculations are only slightly elongated by about 0.003 Å, while the values of the vxz_1 and avxz_1 calculations (which do not converge) are contracted up to 0.013 Å. The CBS limits of both vxz_s and avxz_s calculations are larger than our best values by 0.06 or 0.07 Å for the GaN or GaN^- species (see Tables I and II). The above observations lead us to the same conclusions as for the Ga_2N and Ga_2N^- species with regards to the importance of including the $3d$ electrons in the correlation and the importance of the BSSE correction. The importance of the $3d$ electrons has been demonstrated also in the relevant InN molecule.¹⁹

Previous calculations^{1,3,4} on the GaN molecule, using RECP or not, MRCISD, MRCPA-4, or DKCCSD(T), give R

TABLE I. Absolute energies E (hartrees), Ga–N distance R (Å), dissociation energies D_e (eV), electron affinities EA (eV), and their BSSE corrected values R_{BSSE} (Å), $D_{e1\text{BSSE}}$ (eV), and EA_{BSSE} (eV) for Ga_2N , Ga_2N^- , GaN , and GaN^- . The $(4s^2 4p^1)_{\text{Ga}}(2s^2 2p^3)_{\text{N}}$ electrons are correlated (s calculations).

Basis sets ^a	$\text{Ga}_2\text{N} (\tilde{X}^2\Sigma_u^+)$								$\text{Ga}_2\text{N}^- (\tilde{X}^1\Sigma_g^+)$					
	$-E$	R	R_{BSSE}	D_{e1}^b	$D_{e1\text{BSSE}}^b$	D_{e2}^c	EA	EA_{BSSE}	$-E$	R	R_{BSSE}	D_{e1}^d	$D_{e1\text{BSSE}}^d$	D_{e2}^e
cc-pVDZ(-PP)	571.323 572	1.8417	1.846	4.815	4.614	3.417	2.242	2.148	571.405 960	1.8527	1.858	7.264	6.969	4.551
cc-pVTZ(-PP)	571.418 265	1.8262	1.828	5.562	5.498	3.720	2.425	2.374	571.507 364	1.8386	1.841	7.910	7.796	4.734
cc-pVQZ(-PP)	571.441 210	1.8253	1.826	5.795	5.773	3.817	2.477	2.448	571.532 249	1.8384	1.840	8.072	8.021	4.754
cc-pV5Z(-PP)	571.448 313	1.8249	1.826	5.878	5.869	3.848	2.504	2.487	571.540 345	1.8383	1.839	8.120	8.095	4.748
CBS limit		1.8250	1.826	5.911	5.91	3.863	2.510	2.50		1.8383	1.839	8.133	8.12	4.751
		± 0.0002		± 0.006	± 0.01		± 0.008	± 0.01				± 0.004	± 0.01	± 0.004
aug-cc-pVDZ(-PP)	571.341 411	1.8498	1.852	5.023	4.927	3.351	2.434	2.403	571.430 854	1.8600	1.863	7.191	7.065	4.414
aug-cc-pVTZ(-PP)	571.425 632	1.8309	1.832	5.689	5.651	3.749	2.483	2.476	571.516 886	1.8434	1.845	7.859	7.813	4.650
aug-cc-pVQZ(-PP)	571.444 326	1.8270	1.828	5.856	5.839	3.837	2.507	2.504	571.536 451	1.8403	1.841	8.040	8.020	4.715
aug-cc-pV5Z(-PP)	571.449 693	1.8256	1.261	5.905	5.899	3.861	2.516	2.515	571.542 166	1.8393	1.840	8.096	8.087	4.733
CBS limit		1.8255	1.826	5.918	5.92	3.866	2.525	2.52		1.8393	1.840	8.114	8.11	4.740
		± 0.0003		± 0.004	± 0.01	± 0.003	± 0.002			± 0.0002		± 0.004	± 0.01	
Expt. ^f							2.506							
							± 0.008							
	$\text{GaN} (X^3\Sigma^-)$							$\text{GaN}^- (X^2\Sigma^+)$				$\text{Ga} (^2P)$	$\text{N} (^4S)$	
	$-E$	R	R_{BSSE}	D_e^g	$D_{e\text{BSSE}}^g$	EA	EA_{BSSE}	$-E$	R	R_{BSSE}	D_e^h	$D_{e\text{BSSE}}^h$	EA	EA
cc-pVDZ(-PP)	312.863 853	2.0547	2.063	1.398	1.304	1.108	1.051	312.904 570	1.8237	1.830	2.713	2.563	-0.208	
cc-pVTZ(-PP)	312.931 800	2.0337	2.036	1.842	1.812	1.411	1.390	312.983 645	1.8131	1.815	3.176	3.124	0.077	
cc-pVQZ(-PP)	312.949 032	2.0371	2.038	1.978	1.968	1.541	1.529	313.005 645	1.8133	1.814	3.318	3.297	0.200	
cc-pV5Z(-PP)	312.954 526	2.0388	2.039	2.030	2.026	1.604	1.598	313.013 468	1.8141	1.815	3.372	3.362	0.262	
CBS limit		2.040	2.038	2.049	2.049	1.650	1.64		1.814	1.815	3.392	3.39	0.308	
			± 0.001	± 0.007	± 0.006	± 0.006	± 0.01				± 0.006	± 0.01	± 0.008	
aug-cc-pVDZ(-PP)	312.883 237	2.0764	2.081	1.672	1.635	1.371	1.333	312.933 629	1.8410	1.845	2.777	2.703	0.266	-0.517
aug-cc-pVTZ(-PP)	312.937 841	2.0465	2.049	1.940	1.924	1.582	1.570	312.995 990	1.8218	1.823	3.209	3.181	0.313	-0.297
aug-cc-pVQZ(-PP)	312.951 313	2.0419	2.043	2.019	2.012	1.629	1.624	313.011 162	1.8174	1.818	3.325	3.313	0.323	-0.223
aug-cc-pV5Z(-PP)	312.955 378	2.0405	2.041	2.045	2.042	1.644	1.642	313.015 784	1.8160	1.817	3.362	3.357	0.326	-0.190
CBS limit		2.0406	2.041	2.055	2.054	1.646	1.644		1.8158	1.816	3.373	3.371	0.326	-0.176
		± 0.0004		± 0.002	± 0.001	± 0.003	± 0.004		± 0.0002		± 0.004	± 0.005		± 0.006
Expt. ⁱ													0.300	<0

^aThe part of the basis set on parenthesis corresponds to Ga, i.e., cc-pVDZ(-PP) means cc-pVDZ-PP_{Ga}/cc-pVDZ_N.

^b $2\text{Ga} (^2P) + \text{N} (^4S)$.

^c $\text{Ga} (^2P) + \text{GaN} (X^3\Sigma^-)$.

^d $\text{Ga} (^2P) + \text{Ga}^- (^3P) + \text{N} (^4S)$.

^e $\text{Ga} (^2P) + \text{GaN}^- (X^2\Sigma^+)$.

^fReference 8.

^g $\text{Ga} (^2P) + \text{N} (^4S)$.

^h $\text{Ga}^- (^3P) + \text{N} (^4S)$.

ⁱReference 21.

TABLE II. Absolute energies E (hartrees), Ga–N distance R (Å), dissociation energies D_{e1} (eV), electron affinities EA (eV), and their BSSE corrected values R_{BSSE} (Å), $D_{e1\text{BSSE}}$ (eV), and EA_{BSSE} (eV) for Ga_2N , Ga_2N^- , GaN , and GaN^- . The $(3d^{10}4s^24p^1)_{\text{Ga}}(2s^22p^3)_{\text{N}}$ electrons are correlated (1 calculations).

Basis sets ^a	$\text{Ga}_2\text{N} (\tilde{X}^2\Sigma_u^+)$							$\text{Ga}_2\text{N}^- (\tilde{X}^1\Sigma_g^+)$				
	$-E$	R	R_{BSSE}	D_{e1}^b	$D_{e1\text{BSSE}}^b$	EA	EA_{BSSE}	$-E$	R	R_{BSSE}	D_{e1}^c	$D_{e1\text{BSSE}}^c$
cc-pVDZ(-PP)	571.369 351	1.8084	1.819	5.101	4.763	2.255	2.160	571.452 206	1.8204	1.832	7.547	7.114
cc-pVTZ(-PP)	571.583 874	1.7769	1.787	6.123	5.802	2.461	2.412	571.674 311	1.7891	1.797	8.491	8.121
cc-pVQZ(-PP)	571.749 412	1.7602	1.776	6.421	6.123	2.508	2.488	571.841 577	1.7730	1.789	8.724	8.406
cc-pV5Z(-PP)	571.927 473	1.7634	1.772	6.435	6.248	2.542	2.530	572.020 879	1.7765	1.785	8.713	8.515
CBS limit			1.770		6.295	2.544	2.54			1.784		8.55
					± 0.017	± 0.015	± 0.01			± 0.001		± 0.02
aug-cc-pVDZ(-PP)	571.395 419	1.8120	1.824	5.429	5.089	2.443	2.410	571.485 186	1.8234	1.836	7.602	7.229
aug-cc-pVTZ(-PP)	571.601 652	1.7751	1.788	6.439	5.960	2.511	2.505	571.693 915	1.7879	1.800	8.632	8.147
aug-cc-pVQZ(-PP)	571.763 404	1.7587	1.777	6.723	6.197	2.533	2.540	571.856 495	1.7720	1.790	8.933	8.414
aug-cc-pV5Z(-PP)	571.936 130	1.7587	1.772	6.627	6.283	2.549	2.556	572.029 806	1.7717	1.785	8.852	8.515
CBS limit			1.771		6.306	2.555	2.564			1.784		8.55
			± 0.001		± 0.013	± 0.007	± 0.002			± 0.001		± 0.01
cc-p(wC)VDZ(-PP) ^d	571.811 392	1.7781	1.786	5.252	4.976	2.279	2.186	571.895 148	1.7906	1.799	7.736	7.367
cc-p(wC)VTZ(-PP) ^d	572.311 746	1.7703	1.773	5.942	5.852	2.454	2.405	572.401 930	1.7826	1.786	8.326	8.186
cc-p(wC)VQZ(-PP) ^d	572.449 204	1.7678	1.769	6.190	6.155	2.511	2.483	572.541 473	1.7803	1.782	8.510	8.447
CBS limit		1.767	1.767	6.33	6.31	2.54	2.53		1.779	1.781	8.59	8.57
Expt. ^e						2.506						
						± 0.008						
	$\text{GaN} (X^3\Sigma^-)$							$\text{GaN}^- (X^2\Sigma^+)$				
	$-E$	R	R_{BSSE}	D_e^f	$D_{e\text{BSSE}}^f$	EA	EA_{BSSE}	$-E$	R	R_{BSSE}	D_e^g	$D_{e\text{BSSE}}^g$
cc-pVDZ(-PP)	312.883 518	2.0305	2.044	1.453	1.321	1.222	1.140	312.928 416	1.7874	1.799	2.866	2.653
cc-pVTZ(-PP)	313.009 111	1.9839	1.998	1.973	1.865	1.593	1.541	313.067 651	1.7612	1.768	3.473	3.313
cc-pVQZ(-PP)	313.096 054	1.9761	1.992	2.099	2.031	1.776	1.708	313.161 331	1.7449	1.758	3.669	3.533
cc-pV5Z(-PP)	313.188 030	1.9806	1.989	2.144	2.097	1.828	1.791	313.255 198	1.7458	1.754	3.708	3.624
CBS limit			1.989		2.12	1.89	1.85			1.752		3.66
			± 0.001		± 0.01	± 0.03	± 0.01			± 0.001		± 0.01
aug-cc-pVDZ(-PP)	312.905 965	2.0466	2.060	1.758	1.655	1.485	1.412	312.960 540	1.8013	1.813	2.973	2.796
aug-cc-pVTZ(-PP)	313.018 560	1.9922	2.009	2.117	1.977	1.771	1.715	313.083 646	1.7651	1.774	3.570	3.374
aug-cc-pVQZ(-PP)	313.101 903	1.9728	1.996	2.209	2.076	1.876	1.799	313.170 833	1.7462	1.761	3.762	3.553
aug-cc-pV5Z(-PP)	313.190 956	1.9761	1.990	2.197	2.113	1.883	1.833	313.260 158	1.7444	1.755	3.756	3.622
CBS limit			1.989		2.127	1.90	1.84			1.752		3.65
			± 0.001		± 0.004	± 0.02	± 0.01			± 0.001		± 0.01
cc-p(wC)VDZ(-PP)	313.103 340	1.9929	2.005	1.496	1.380	1.317	1.243	313.151 749	1.7523	1.762	3.018	2.828
cc-p(wC)VTZ(-PP)	313.374 430	1.9840	1.988	1.921	1.882	1.596	1.568	313.433 072	1.7484	1.752	3.446	3.379
cc-p(wC)VQZ(-PP)	313.448 654	1.9840	1.986	2.057	2.043	1.729	1.716	313.512 207	1.7476	1.749	3.595	3.568
CBS limit		1.984	1.985	2.12	2.12	1.85	1.84		1.747	1.748	3.68	3.67
Expt.												

^aThe part of the basis set in parentheses corresponds to Ga, i.e., cc-pVDZ(-PP) means cc-pVDZ-PP_{Ga}/cc-pVDZ_N; cc-p(wC)VQZ(-PP) means cc-pwCVQZ-PP_{Ga}/cc-pVQZ_N.

^b2Ga(²P)+N(⁴S).

^cGa(²P)+Ga(³P)+N(⁴S).

^dThe D_{e2} values for Ga_2N with respect to $\text{Ga}(\text{}^2P)+\text{GaN}(X^3\Sigma^-)$ are 3.756 (x=D), 4.022 (T), 4.133(Q), 4.21 (CBS) eV. The D_{e2} values for Ga_2N^- with respect to $\text{Ga}(\text{}^2P)+\text{GaN}^-(X^2\Sigma^+)$ are 4.718 (x=D), 4.880 (T), 4.915 (Q), 4.92 (CBS) eV.

^eReference 8.

^fGa(²P)+N(⁴S).

^gGa(³P)+N(⁴S).

values ranging from 1.964 to 2.060 Å compared to our 1.985 Å value. All previous calculations were carried out with smaller basis sets compared to ours of quintuple zeta quality and those which had a basis set of quadruple zeta quality did not correlate the 3d electrons of the Ga atom. For the GaN^- anion, Denis and Balasubramanian⁴ give $R = 1.740$ Å, which is very close to our best value of 1.748 Å.

Dissociation energies. The dissociation energies D_{e1} of $\text{Ga}_2\text{N}(\tilde{X}^2\Sigma_u^+)$ with respect to the atomic products $2\text{Ga}(\text{}^2P)+\text{N}(\text{}^4S)$ is 6.31 eV [CBS limit of wcvxz_1(BSSE) calculation] and D_{e2} with respect to the $\text{GaN}(X^3\Sigma^-)+\text{N}(\text{}^4S)$ is 4.21 eV (CBS limit of wcvxz_1 calculation) (see Table II). For the $\text{Ga}_2\text{N}^-(\tilde{X}^1\Sigma_g^+)$ anion, the corresponding quantities

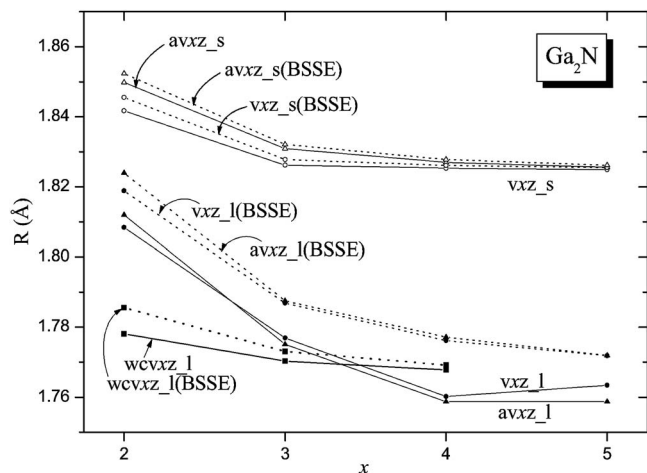


FIG. 1. RCCSD(T) bond distance $R(\text{Ga}-\text{N})$ of Ga_2N ($\tilde{X}^2\Sigma_u^+$) with respect to basis set size x , $x=2$ (double), 3(triple), 4(quadruple), 5(quintuple) for three types of basis sets, i.e., cc-pVxZ-PP_{Ga}/cc-pVxZ_N (vxz), aug-cc-pVxZ-PP_{Ga}/aug-cc-pVxZ_N (avxz), and cc-pwCVxZ-PP_{Ga}/cc-pVxZ_N (wcvxz) correlating 11 electrons (s) or 31 electrons (l), without or with BSSE corrections (BSSE).

are $D_{e1}=8.57$ eV with respect to $\text{Ga}(^2P)+\text{Ga}^{-}(^3P)+\text{N}(^4S)$ and $D_{e2}=4.92$ eV with respect to the $\text{GaN}^{-}(X^2\Sigma^+)+\text{N}(^4S)$. Wang and Balasubramanian⁵ did a CCSD(T) single point calculation for the Ga_2N molecule and found $D_{e1}=6.47$ eV close enough to our best CBS limit of 6.31 eV.

For the GaN and GaN^{-} species, our best CBS limits of the D_e values are 2.12 and 3.67 eV, respectively (see Table II). Previous calculations^{1,3,4} on the GaN molecule, using RECP or not, MRCISD, MRCPA-4, or DKCCSD(T), gave D_e values smaller than ours ranging from 1.86 to 2.08 eV.

The depictions of the D_{e1} of Ga_2N and D_e of GaN with respect to the size of the three basis sets, for two different numbers of correlated electrons and with or without BSSE corrections, are shown in Figs. 3 and 4, respectively. Both figures have similar shapes. As can be seen from these figures and Table II, the CBS values of the wcvxz_l(BSSE), wcvxz_l, vxz_l(BSSE) and avxz_l(BSSE) calculations for

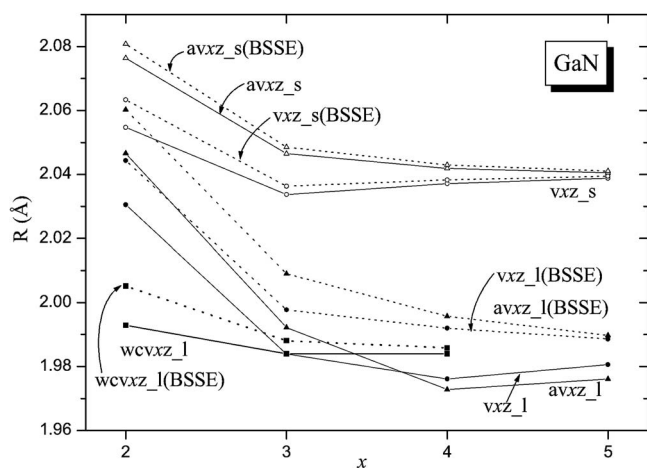


FIG. 2. RCCSD(T) bond distance $R(\text{Ga}-\text{N})$ of GaN ($X^3\Sigma^-$) with respect to basis set size x , for three types of basis sets, i.e., cc-pVxZ-PP_{Ga}/cc-pVxZ_N (vxz), aug-cc-pVxZ-PP_{Ga}/aug-cc-pVxZ_N (avxz), and cc-pwCVxZ-PP_{Ga}/cc-pVxZ_N (wcvxz) correlating 8 electrons (s) or 18 electrons (l), without or with BSSE corrections (BSSE).

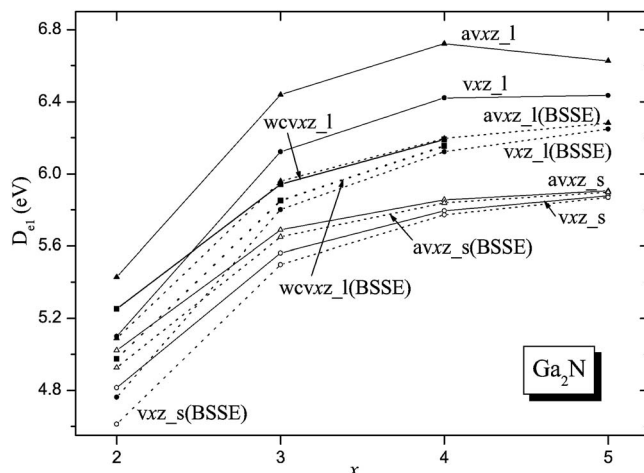


FIG. 3. RCCSD(T) dissociation energy with respect to the atomic products, D_{e1} of Ga_2N ($\tilde{X}^2\Sigma_u^+$) vs basis set size x , for three types of basis sets, i.e., cc-pVxZ-PP_{Ga}/cc-pVxZ_N (vxz), aug-cc-pVxZ-PP_{Ga}/aug-cc-pVxZ_N (avxz), and cc-pwCVxZ-PP_{Ga}/cc-pVxZ_N (wcvxz) correlating 11 electrons (s) or 31 electrons (l), without or with BSSE corrections (BSSE).

all D_{e1} , D_{e2} , and D_e for each of all four species, Ga_2N , Ga_2N^{-} , GaN, and GaN^{-} are almost identical; they do not differ by more than 0.02 eV. In contrast, in all four species, the values of the vxz_l and avxz_l calculations (which do not converge) are larger than the CBS limit of the wcvxz_l by up to 0.4 eV for $x=4$ or 5. This fact shows clearly the importance of the BSSE correction when the basis set is not appropriate for the number of electrons which are correlated. The CBS limits of both vxz_s and avxz_s calculations are smaller than the best values by up to 0.4 eV (see Tables I and II), showing the importance of the inclusion of the 3d electrons in the correlation energy.

Electron affinities. Previously calculated EA values of Ga_2N , which varied over a wide range from 1.52 to 2.36 eV, made a systematic theoretical study of EA necessary and challenging. Wang and Balasubramanian⁵ did B3LYP, MP2, CCD, CASSCF, and single point MRSDCI(+Q) calculations

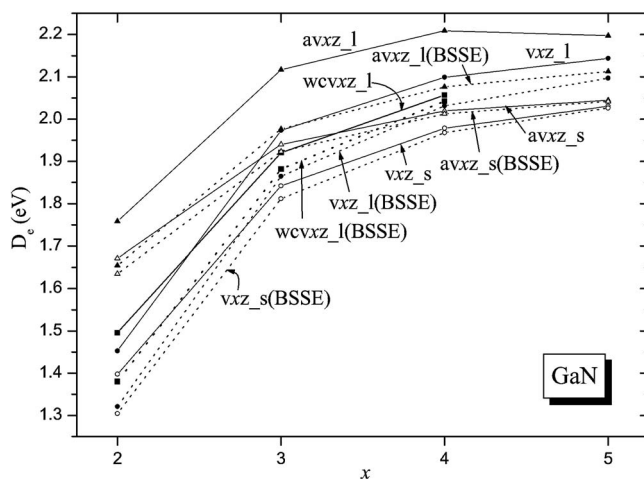


FIG. 4. RCCSD(T) dissociation energy D_e of GaN ($X^3\Sigma^-$) with respect to basis set size x , for three types of basis sets, i.e., cc-pVxZ-PP_{Ga}/cc-pVxZ_N (vxz), aug-cc-pVxZ-PP_{Ga}/aug-cc-pVxZ_N (avxz), and cc-pwCVxZ-PP_{Ga}/cc-pVxZ_N (wcvxz) correlating 8 electrons (s) or 18 electrons (l), without or with BSSE corrections (BSSE).

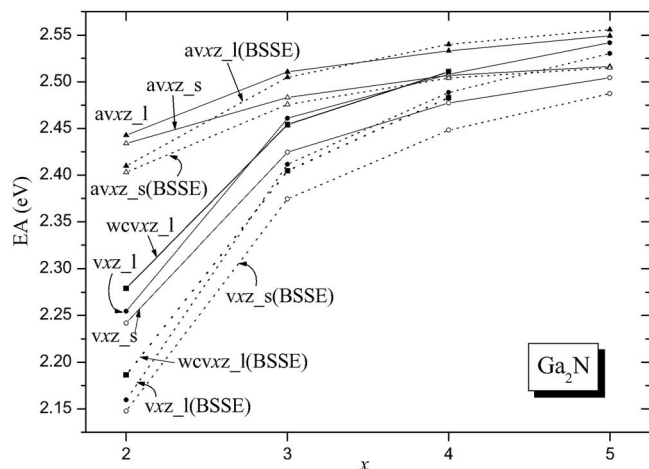


FIG. 5. RCCSD(T) electron affinity EA of Ga_2N with respect to basis set size x , for three types of basis sets, i.e., cc-pVxZ-PP $_{\text{Ga}}$ /cc-pVxZ $_{\text{N}}$ (vxz), aug-cc-pVxZ-PP $_{\text{Ga}}$ /aug-cc-pVxZ $_{\text{N}}$ (avxz), and cc-pwCVxZ-PP $_{\text{Ga}}$ /cc-pVxZ $_{\text{N}}$ (wcvxz) correlating 11 electrons (s) or 31 electrons (l), without or with BSSE corrections (BSSE).

using a medium core RECP for Ga and N, a double zeta quality basis set for the $3d4s4p$ electrons of Ga and $2s2p$ electrons of N and they kept the $3d$ electrons inactive. Their EAs were 1.99, 1.96, 1.80, 1.52, and 1.72(1.68) eV, respectively. Sheehan *et al.*⁸ did a density functional theory calculation and found an EA of 2.36 eV at the B3LYP/aug-cc-pVDZ level close enough to their experimental value of 2.506 ± 0.008 eV (Ref. 8) and to our theoretical value of 2.53 eV (see below).

The EA of the Ga_2N molecule is given in Tables I and II and it is depicted in Fig. 5. Our best CBS limit is that of the wcvxz_l(BSSE) calculations, 2.53 eV, which is in very good agreement with the experimental value of Sheehan *et al.*,⁸ 2.506 ± 0.008 eV (photoelectron spectroscopy). It is interesting that all eight types of calculations converged to similar CBS limits ranging from 2.51 to 2.56 eV. In the case of the vxz_l and avxz_l calculations, the results are good because

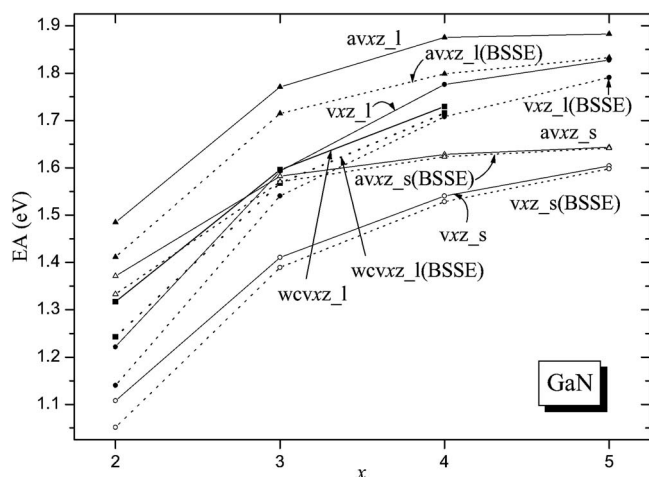


FIG. 6. RCCSD(T) electron affinity EA of GaN with respect to basis set size x , for three types of basis sets, i.e., cc-pVxZ-PP $_{\text{Ga}}$ /cc-pVxZ $_{\text{N}}$ (vxz), aug-cc-pVxZ-PP $_{\text{Ga}}$ /aug-cc-pVxZ $_{\text{N}}$ (avxz), and cc-pwCVxZ-PP $_{\text{Ga}}$ /cc-pVxZ $_{\text{N}}$ (wcvxz) correlating 8 electrons (s) or 18 electrons (l), without or with BSSE corrections (BSSE).

both Ga_2N and Ga_2N^- species present the same BSSE, resulting in the elimination of the errors. It seems that the inclusion of the $3d$ electrons correlation is unnecessary, but this is not known *a priori*.

For GaN , previous work of Denis and Balasubramanian⁴ gave an estimated EA of 1.44 ± 0.5 eV with a large error bar. Our best result of the EA is 1.84 eV. This number corresponds to the CBS limit of the wcvxz_l(BSSE), wcvxz_l, vxz_l(BSSE), and avxz_l(BSSE) calculations (see Table II and Fig. 6). The vxz_l and avxz_l calculations converge to CBS values only because the BSSEs of the calculations on the GaN and GaN^- species are almost counterbalanced. However, they are enlarged by 0.05 eV, while the CBS limits of both vxz_s and avxz_s calculations are smaller by 0.2 eV.

IV. CONCLUSIONS

Since previous theoretical EA values of Ga_2N and GaN cover a wide range and the accurate calculation of the EA is a challenge, we carried out RCCSD(T) calculations on both neutral GaNGa and GaN as well as their negative ions, employing a series of basis sets (from double to quintuple zeta quality) augmented or not, weighted core or not, correlating the $(2s^22p^3)_{\text{N}}+(4s^24p^1)_{\text{Ga}}$ or $(2s^22p^3)_{\text{N}}+(3d^{10}4s^24p^1)_{\text{Ga}}$ electrons, and taking into account the BSSE corrections or not. Our conclusions are summarized as follows:

- (1) (a) For the $\text{Ga}_2\text{N}(\tilde{X}^2\Sigma_u^+)$ molecule, our final values for the bond distances, the dissociation energies with respect to the atomic products (D_{e1}) and to $\text{GaN}+\text{Ga}$ (D_{e2}), and the EA are $R_{\text{Ga-N}}=1.767$ Å, $D_{e1}=6.31$ eV, $D_{e2}=4.21$ eV, and EA=2.53 eV. The last value is in excellent agreement with the experimental value of 2.506 ± 0.008 eV.⁸ (b) For the $\text{Ga}_2\text{N}^-(\tilde{X}^1\Sigma_g^+)$ anion, the corresponding values are $R_{\text{Ga-N}}=1.781$ Å, $D_{e1}=8.57$ eV (with respect to $\text{Ga}+\text{Ga}^-+\text{N}$), and $D_{e2}=4.92$ eV (with respect to GaN^-+Ga). (c) For the diatomic species, our final results are $R_{\text{Ga-N}}=1.985$ Å, $D_e=2.12$ eV, and EA=1.84 eV for $\text{GaN}(X^3\Sigma^-)$, and $R_{\text{Ga-N}}=1.748$ Å and $D_e=3.67$ eV for $\text{GaN}^-(X^2\Sigma^+)$.
- (2) The inclusion of the $3d$ electron correlation is necessary. There are significant differences in the calculated R and D_e values in all systems investigated and in the EA of GaN , between the results obtained when the $3d$ electrons are correlated and those without the $3d$ electrons correlated. In the case of the EA of Ga_2N , the correlation of $3d$ electrons seems unnecessary only because of cancellation of errors.
- (3) It is necessary to use a basis set developed for correlating the $3d$ electrons. The use of basis sets, irrespective of size, developed for fewer correlated electrons results in overestimation or underestimation of calculated quantities which do not converge as a function of basis set quality.²⁰ BSSEs are then large, as observed in the present study, yet, in strongly bound systems such corrections are customarily ignored. This study shows that BSSE corrections in these cases do yield the correct values.

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