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Spectroscopic constants and potential energy curves of gallium nitride (GaN) and ions: GaN^+ and GaN^-

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Abstract

Electronic states of GaN and their ions are studied by employing multi-reference configuration interaction (MRCI) and relativistic DKCCSD(T) calculations. The $^3\Sigma^-$ state is 532 cm^{-1} below the $^3\Pi$ state using MRCI, whereas the DKCCSD(T)/CBS energy separation is 857 cm^{-1}. The low lying excited states undergo curve crossing with the dissociative $^5\Sigma^-$ and $^5\Pi$ states causing predissociation. For GaN^-, the ground state is $^2\Sigma^+$ and an electron affinity of 1.44 ± 0.5 eV with an excited $^2\Pi$ state at 662 cm^{-1}. GaN^+ is weakly bound with an IP of 7.88 eV. The dissociation energy of GaN is 46.5 ± 1 kcal/mol.

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1. Introduction

During the last decade Group 13 nitrides, especially those composed of gallium, have attracted the attraction of material scientists due to their importance in nanotechnology, blue lasers, and semiconductors [1–6]. Due to their important applications in laser systems several attempts have been made to synthesize nanotubes composed by Group 13 nitrides. Successful synthesis of BN [4], and GaN [5] nanotubes have been possible quite recently, and the theoretical characterization of those nanotubes was recently performed by Chen et al. [3]. Spectroscopy and electronic states of BN have been the topics of several theoretical [7–9] and experimental [10] studies. Lee et al. [7] have investigated BN employing MRSDCI and CCSD(T) methodologies. The results showed that there are two nearly degenerate states, $^3\Pi$ and $^1\Sigma^+$, separated only by 381 cm^{-1}. Analogous AlN, has also been studied [11] which showed similarity to BN. Two nearly degenerate states, $X^3\Pi$ and $^3\Sigma^-$, separated by only 400 cm^{-1} were found for AlN [11]. A recent study [12] confirmed this by employing MRSDCI methodologies and large basis sets.

In spite of the importance of GaN, it has received less attention than the other Group 13 nitrides. At present, there is no experimental investigation of GaN although two theoretical studies have been carried out [6,14]. The ground and first excited states were characterized by Mochizuki and Tanaka [14] employing the fourth-order muti-reference coupled pair approximation. Most recently Uneo and co-workers [6] have investigated the ground and 22 excited states of GaN at the MRSDCI/aug-cc-pVQZ level of theory.

In the present Letter, we have investigated the ground and low lying excited states of GaN up to 50 000 cm^{-1} by employing MRSDCI methodologies. We have also studied the low lying states of their ions for the first time. For comparative purposes we have performed coupled cluster calculations on the $^3\Sigma^-$, $^3\Pi$ and $^1\Sigma^+$ states. The most accurate determination, up to date, of the dissociation energy of

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GaN has been performed, since it is a datum required in the chemical vapor deposition, commonly used to produce thin films of GaN [1,2]. Finally, since we have employed MRSDCI methodologies with ECPs [15–18] to compare with all-electron results which showed that the results obtained using ECPS are quite accurate and thus it is feasible to obtain accurate results on larger GaN clusters [19]. Spectroscopy of such clusters using mass-selected method in Ar matrices have been the topic of active studies [20] as well as by laser ablation methods [21] and applications to semiconductor clusters like the ones studied here are underway.

2. Methods

We have performed the initial calculations employing the CASSCF method to generate the orbitals for the MRSDCI computations. The CASSCF method included a full CI space of configurations obtained by distributing all eight valence electrons among the Ga 3s, 3p, N 2s and 2p orbitals in all possible ways. The MRSDCI calculations included all CASSCF configurations with absolute coefficients higher than 0.0005. We carried out point-wise optimizations at the MRSDCI level. Then a numerical fitting procedure was employed to fit all the energy points to potential curves from which various spectroscopic constants were then deduced. The correlation effects originating from the 3d electrons could be important for gallium compounds [13]. Therefore, we have performed CASSCF calculations that included the 10 3d electrons of gallium in the active space. These calculations were employed to select the configurations for further MRSDCI calculations with a threshold of 0.01. These calculations including the d electrons were performed for the $^{3}\Sigma^{-}$ and $^{1}\Sigma^{+}$ states.

Table 2
Spectroscopic constants of various electronic states of GaN calculated at the MRSDCI level

State	T_e (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	μ_e (D)
$^{3}\Sigma^{-}$(I)	0.0	1.964	530	1.75
$^{3}\Pi$(I)	532	1.828	635	2.06
$^{1}\Sigma^{+}$(I)	6135	1.691	816	3.52
$^{1}\Pi$(I)	8318	1.789	699	2.95
$^{1}\Delta$(I)	12 343	1.950	559	1.30
$^{1}\Delta$(II)	13 427	1.953	510	0.91
$^{1}\Sigma^{+}$(II)	20 056	1.916	631	2.15
$^{3}\Sigma^{+}$(I)	21 197	1.686	774	2.71
$^{3}\Pi$(II)	26 013	1.807	642	1.93
$^{3}\Pi$(II)′	26 337	2.453	326	1.39
$^{3}\Pi$(III)	30 604	2.099	614	0.52
$^{1}\Pi$(II)	30 768	1.943	516	1.74
$^{3}\Sigma^{+}$(II)	34 792	1.909	543	2.06
$^{5}\Sigma^{+}$(I)	38 194	1.855	607	0.84
$^{5}\Delta$(I)	43 533	1.836	659	1.58
$^{5}\Pi$(II)	45 368	2.178	425	0.41
$^{5}\Delta$(II)	45 568	1.844	706	1.68
$^{5}\Sigma^{-}$(II)	48 393	1.849	693	2.10

Table 1
Spectroscopic constants for the $^{3}\Sigma^{-}$, $^{3}\Pi$ and $^{1}\Sigma^{+}$of GaN obtained at different levels

Method	Electrons correlated	Basis set	T_e (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	μ (D)
	$^{3}\Sigma^{-}$					
MRSDCI	8	Ga(4s4p2d1f)/C(4a4p1d)	0.0	1.964	530	1.75
MRSDCI	18	Ga(4s4p5d2f)/C(4a4p2d1f)	0.0	1.995	543	1.91
MRSDCI+Q	18	Ga(4s4p5d2f)/C(4a4p2d1f)	0.0	1.982	521	
DKCCSD(T)	8	DKTZ	0.0	2.055	532	2.00
DKCCSD(T)	8	DKQZ	0.0	2.058		2.26
DKCCSD(T)	8	∞	0.0	2.060		
DKCCSD(T)	25	∞	0.0	2.009		
MRSDCI[a]	8	aug-cc-pVQZ	0.0	2.021	502	
	$^{3}\Pi$					
MRSDCI	8	Ga(4s4p2d1f)/C(4a4p1d)	532	1.828	635	2.06
DKCCSD(T)	8	DKTZ	1578	1.925	623	2.35
DKCCSD(T)	8	DKQZ	1542	1.925		2.48
DKCCSD(T)	8	∞	1502	1.925		
DKCCSD(T)[a]	25	∞	857	1.862		
MRSDCI[b]	8	aug-cc-pVQZ	645	1.873	622	
	$^{1}\Sigma^{+}$					
MRSDCI	8	Ga(4s4p2d1f)/C(4a4p1d)	6135	1.691	816	3.52
MRSDCI	18	Ga(4s4p5d2f)/C(4a4p2d1f)	5850	1.686	835	3.64
MRSDCI+Q	18	Ga(4s4p5d2f)/C(4a4p2d1f)	6321	1.690	799	
DKCCSD(T)	8	DKTZ	7650	1.764	788	3.83
DKCCSD(T)	8	DKQZ	7408	1.761		3.97
DKCCSD(T)	8	∞	7230	1.759		
DKCCSD(T)[a]	25	∞	6408	1.699		
MRSDCI[b]	8	aug-cc-pVQZ	6452	1.751	780	

[a] Core correction obtained at the CCSD(T)/cc-pwCVTZ level of theory.

[b] Results taken from Ref. [6].

Relativistic effective core potentials (RECP) for gallium and N [15–18] were employed with the $4s^{2}4p^{1}$ orbitals of

Ga and the $2s^22p^3$ of Nitrogen, and also the ones with $3d^{10}4s^24p^1$ of Ga in valence. For the smaller active space the original 3s3p basis for gallium was augmented by another set of even-tempered functions, plus two 3d and one set of 4f functions. The exponents for the 3d functions were chosen as 0.9131 and 0.2514, and 0.45 for the 4f functions. For the larger active space that included the d electrons we started with the 3s3p4d set and added one s, p, and d functions and two sets of 4f functions with exponents, 0.181 and 0.47. For Nitrogen we employed the 4s4p basis set with one d function with exponent 0.8 and for the calculations that included the 3d electrons in the active space, the basis set of Nitrogen was extended to 4s4p2d1f, with exponents of the d functions of 1.6540 and 0.4649, and with f function exponent of 1.0930.

The initial MRSDCI calculations indicated that the leading configurations of the $^3\Sigma^-$ and $^1\Sigma^+$, $^3\Pi$ states are dominated by a single reference, 0.93 in $^3\Sigma^-$, 0.88 in $^1\Sigma^+$, and 0.92 for the $^3\Pi$ states. Therefore, it is expected that DKCCSD(T) calculations [22,23] performed for these states to be accurate. The selected basis sets for those calculations are the cc-pVXZ_DK X = T,Q basis sets [23]. The cc-pVXZ_DK basis sets [23] are contracted from the original cc-pVXZ basis sets [24,25]. Extrapolation to the CBS limit was accomplished by employing the two parameter equation suggested by Halkier et al. [26]. We evaluated the importance of core correlation as the difference between full and frozen core CCSD(T) calculations. We correlated the valence and the next inner shells, that is, the 3s 3p and 3d electrons of Gallium and 1s of nitrogen. For nitrogen we employed the cc-pwCVTZ basis set [24] and for Ga we started with the cc-pVTZ basis set [25] to which we added, 2s, 2p, 2d, 2f, and one g functions. The exponents were 0.3660 and 2.1959 for the s functions, 0.5088 and 1.0888 for the p functions, 0.8461 and 2.3369 for the d functions, 1.1063 and 4.4252 for the f functions and 1.35 for the g

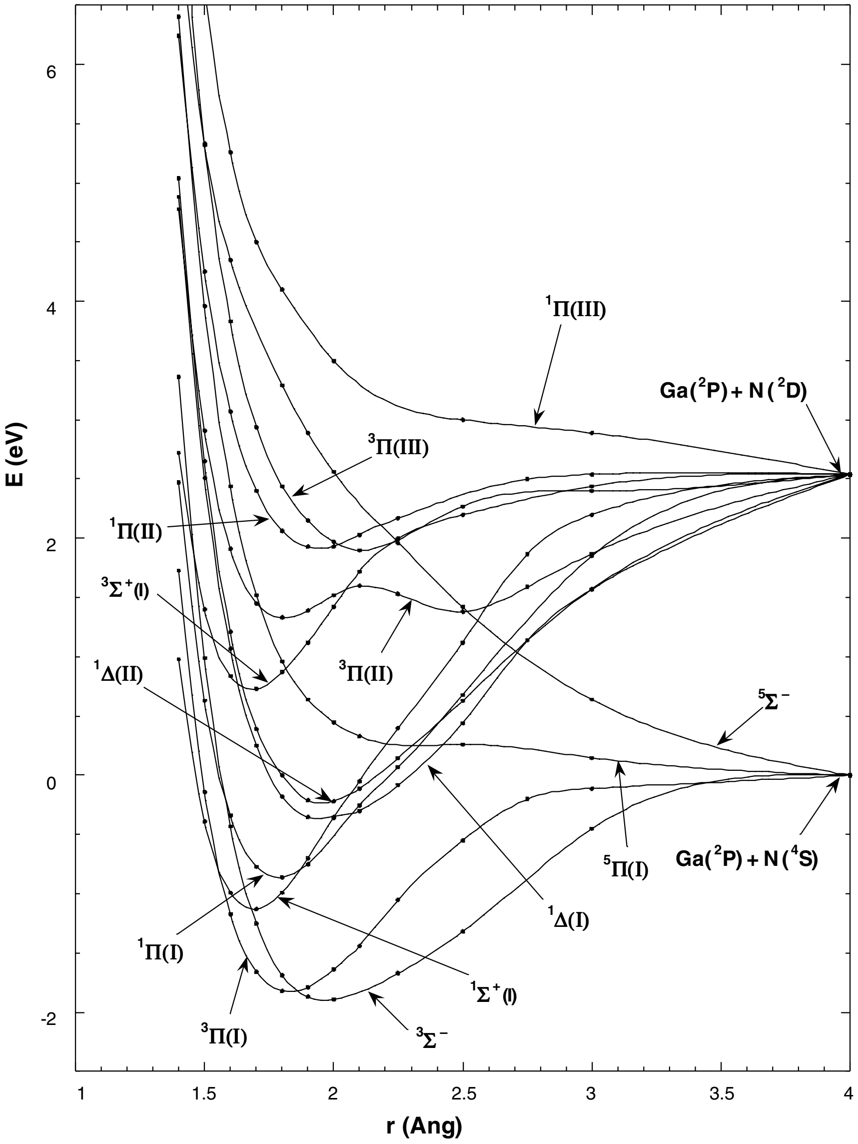

Fig. 1. Potential Energy curves for the low lying excited states of GaN that dissociates in to the two lowest asymptotes.

functions. Therefore, our basis set for Ga is of cc-pwCVTZ quality. The coupled cluster calculations were performed employing GAUSSIAN '03 [27] and all MRSDCI calculations with a modified version [28] of ALCHEMY 2002[1,2]. The Davidson correction [29] (noted as MRSDCI + Q) which takes into consideration the effect of unlinked quadruple clusters was included. Similar techniques and basis sets have been employed before for larger related clusters [30].

3. Results and discussions

3.1. Ground state

In Table 1, we have presented the spectroscopic constants obtained for the three lowest lying states of GaN at the MRSDCI and CCSD(T) levels as a function of basis sets and number of correlated electrons. All the methodologies employed support a $^3\Sigma^-$ ground state. At the MRSDCI level, employing the smaller basis set and without including the correlation due to 3d electrons, the splitting between the ground state and the low lying $^3\Pi$ state is 532 cm^{-1}. As expressed above, the leading configurations of the MRSDCI expansion have a coefficient larger that 0.9, therefore it is expected that the CCSD(T) results are accurate enough to determine the ground state of GaN. The adequacy of the CCSD(T) methodology is also indicated by a small T1 diagnostic [19]; it is smaller than the recommended threshold, 0.018. The DKCCSD(T) calculations extrapolated to the complete basis set limit indicate that the ground state of GaN is $^3\Sigma^-$, although the separation of the first excited state is larger 1522 cm^{-1}. That splitting is substantially reduced when 3s, 3p, 3d core correlations are correlated. The estimated splitting including the core correction is 857 cm^{-1}, in good agreement with our MRSDCI result of 532 cm^{-1}. The results see to indicate some fortuitous degree of error cancellation between the basis set incompleteness and correlation effects in the MRSDCI results. We have also investigated for the $^1\Sigma^+$ state further. In Table 1, we report the T_e for the $^1\Sigma^+$ state employing three different procedures. The agreement among various procedures is very good. The MRSDCI results including the 3d electrons in the active space predict a splitting of 5850, only 285 cm^{-1} lower than the MRSDCI results without including the d electrons in the active space. At the DKCCSD(T) level of theory the effect of core correlation reduces the splitting by 822 cm^{-1}. Therefore, we have confirmed that large part of core correlation is being canceled in our MRSDCI calculations without the 3d electrons in the active space. The DKCCSD(T) method yields 6408 cm^{-1} whereas at the MRSDCI+Q level including the d electrons it is 6321 cm^{-1}. The agreement between MRSDCI and DKCCSD(T) is also good for the vibrational frequencies and bond lengths. The observed contraction of the bond length due to the core correlation, evaluated at the CCSD(T) level of theory is 0.051 Å for the ground state, and for the $^3\Pi$ and $^1\Sigma^+$ states it is 0.063 and 0.060 Å, respectively.

Several investigations were performed on BN [7–9]. In all investigations, the CCSD(T) methodology incorrectly predicted the ground state of BN, placing the $^1\Sigma^+$ state above the $^3\Pi$ state. The inclusion of iterative triple excitations yields reliable results [7–9] and it is expected that quadruple results give the same T_e as determined by multi-reference methodologies [9]. Bartlett and co-workers [31] have reported CCSD(T) calculations for AlN by employing large ANO's basis set. For AlN the splitting between the $^3\Sigma^+$ and $^3\Pi$ states was only 20 cm^{-1}, with the $^3\Sigma^+$ as ground state in contrast to the MRSDCI results of Bauschlicher and Partridge [8] that predicted the $^3\Pi$ state as ground state by 371 cm^{-1}. Thus, GaN is the first Group 13 nitride for which CCSD(T) yields reliable results.

3.2. Electronic Spectrum

We present in Table 2, a more extensive study of 17 low lying excited states of GaN. In Fig. 1, we report the potential energy curves of the low lying excited states that dissociate into the lowest two asymptote [18], Ga(^{2}P) + N(^{4}S) and Ga(^{2}P) + N(^{2}D). As seen from Fig. 1 the repulsive curves $^5\Sigma^-$, and $^5\Pi$ dissociating to the ground state [18] Ga(^{2}P) + N(^{4}S) atoms intersect with all the potential

Table 3
Spectroscopic constants of the potential curves of various electronic states of GaN$^+$ and GaN$^-$ calculated at the MRSDCI level

	Method	T_e (cm^{-1})	r_e (Å)	ω_e (cm^{-1})
GaN$^-$				
$^2\Sigma^+$(I)	MRSDCI	0.0	1.740	750
$^2\Pi$(I)	MRSDCI	662	1.815	676
$^4\Sigma^+$	MRSDCI	14 785	1.913	524
$^4\Pi$(I)	MRSDCI	14 957	2.047	431
$^4\Delta$	MRSDCI	18 912	1.941	684
$^2\Sigma^+$(II)	MRSDCI	20 289	1.776	642
$^4\Sigma^-$(I)	MRSDCI	21 287	1.995	537
$^2\Delta$	MRSDCI	21 697	1.982	487
$^4\Sigma^-$(II)	MRSDCI	26 778	1.931	478
GaN$^+$				
$^4\Sigma^-$(I)	MRSDCI	0.0	2.914	77
	CCSD(T)/ATZ[a]	0.0	2.912	86
	CCSD(T)/AQZ[b]	0.0	2.865	
$^2\Delta$(I)	MRSDCI	15 158	1.939	507
$^2\Pi$(I)	MRSDCI	15 814	1.787	666
$^2\Delta$(II)	MRSDCI	21 339	2.092	266
$^2\Sigma^-$	MRSDCI	21 460	2.104	228
$^2\Sigma^+$	MRSDCI	28 621	1.970	365
$^4\Pi$(I)	MRSDCI	28 923	1.752	742
$^4\Sigma^-$(II)	MRSDCI	34 629	1.971	585
$^4\Pi$(II)	MRSDCI	45 464	2.042	692

[a] ATZ denotes aug-cc-pVTZ basis set.
[b] AQZ denotes aug-cc-pVQZ basis set.

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[1] Major Authors of ALCHEMY II are M. Yoshimine, B. Liu and B. Lengsfield.

[2] ALCHEMY 2002, Modified and Enhanced Version by K. Balasubramanian.

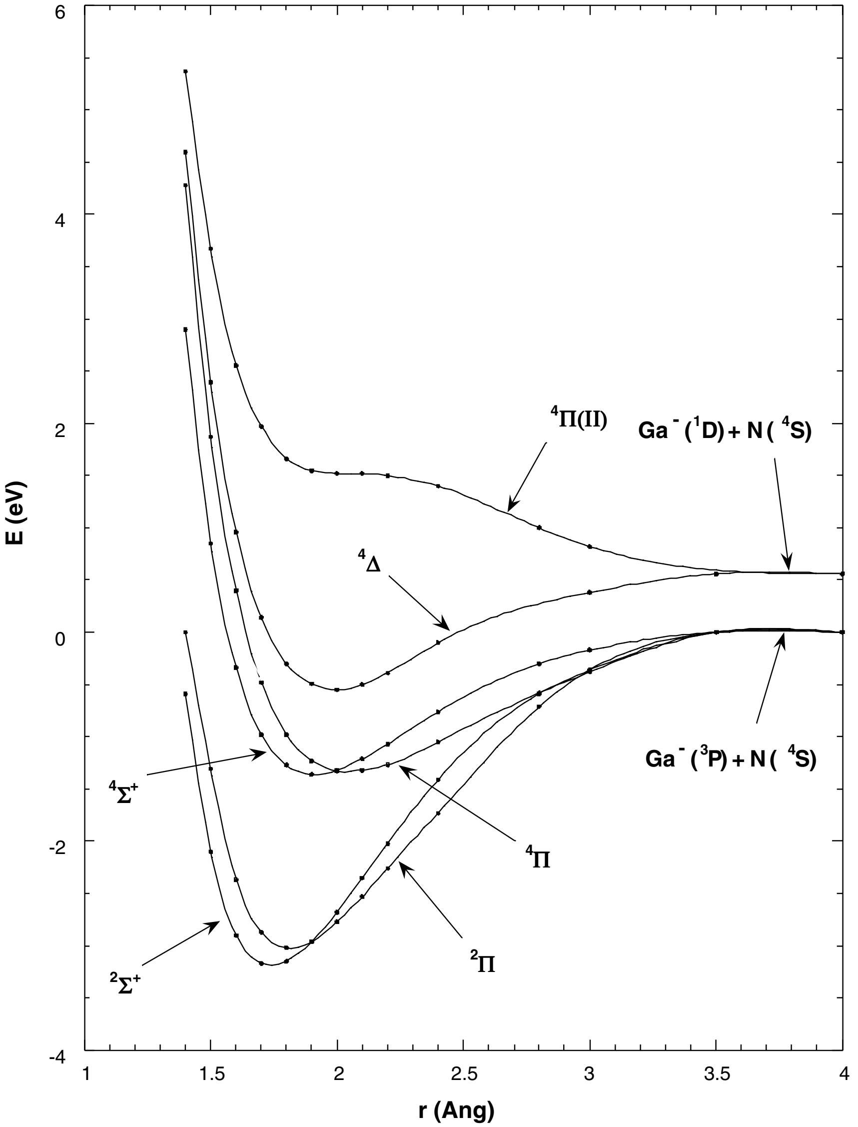

Fig. 2. Potential Energy curves for the low lying excited states of GaN$^-$.

energy curves reported in Fig. 1. The intersections of the $^5\Sigma^-$ curve with the excited $^3\Pi$(II) and $^3\Pi$(III) are especially interesting. Since the $^5\Sigma^-$ state gives rise to $\Omega = 2$, 0^- and 1 states the intersection of $^5\Sigma^-$ with the $^3\Pi$(III) state will cause the mixing of $^3\Pi_{0-}$, $^3\Pi_2$, $^3\Pi_1$ with the corresponding spin orbit components of $^5\Sigma^-$ states through spin orbit coupling. Thus, the only state that can survive predissociation by the $^5\Sigma^-$ repulsive state is the $\Omega = 0^+$ of the $^3\Pi$(III) state. The $^3\Pi$(II) state presents a double minimum as shown in Fig. 1. The later state crosses both dissociative states $^5\Sigma^-$ and the $^5\Pi$, in contrast to the $^3\Pi$(III) that only interacts with the $^5\Sigma^-$, because of its higher T_e. The $^5\Pi$ state gives rise to $\Omega = 3$,2, and 1(2), 0^-, 0^+, states. The interaction with the spin orbit state of $^3\Pi$(II) state will cause the mixings of the spin–orbit components, and none of the spin–orbit states will survive predissociation. Therefore, future experimental observation of the bands $^3\Pi(\text{II}) \rightarrow {}^3\Sigma^-$ will be very interesting.

3.3. GaN$^-$ and GaN$^+$

Table 3 shows the spectroscopic constants of GaN$^-$ and GaN$^+$. The ground state of GaN$^-$ is expected to be $^2\Sigma^+$, although there is a very low lying excited state $^2\Pi$, 662 cm^{-1} above the ground state. These results are in agreement with our previous investigation [13] of GaAs$^-$. In that case the separation between those two states was higher, 936 cm^{-1}. The electronic configuration of the ground state of GaN$^-$ is $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4$, and the coefficient of the leading configuration is 0.89. The contraction of the bond length with respect to the ground state is about 0.25 Å. In Fig. 2 we show the potential energy curves for the low lying excited states of GaN$^-$. The other excited states of GaN$^-$ investigated in the present Letter lie at somewhat higher T_e's. The next two states are nearly degenerate, $^4\Sigma^+$ and $^4\Pi$ and are 15 000 cm^{-1} above the ground state. Due to strong spin contamination in the

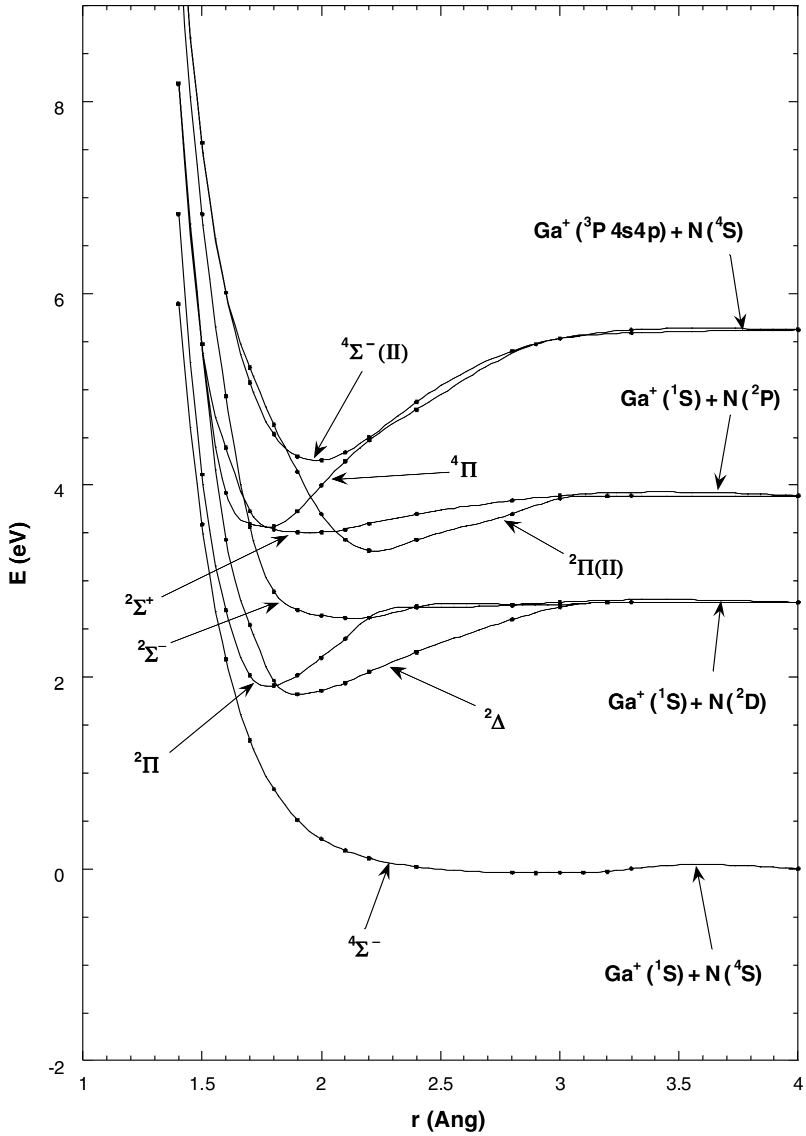

Fig. 3. Potential Energy curves for the low lying excited states of GaN^+.

UHF wavefunction, CCSD(T) was not feasible for GaN^-. Our raw estimate of the electron affinity of GaN employing MRSDCI methodologies with a small basis set is 1.44 eV.

In Fig. 3, we report the potential energy curves for the low lying excited states of GaN^+. The ground state is $^4\Sigma^-$ in agreement with our results obtained for $GaAs^+$. In that case, the first excited state was $^2\Pi$, and it was found at 10 500 cm^{-1}. For GaN^+ the $^2\Pi$ state lies at around 15 000 cm^{-1}. The $^4\Sigma^-$ state is only slightly bound. This is indicated by a long bond distance 2.914 Å and a low vibrational frequency, 77 cm^{-1}. The dissociation energy of the $^4\Sigma^-$ state is only 1.91 kcal/mol, which suggests a van der Waals interaction. Since the IP of Ga is lower than N, most of the ionization takes place at Ga, thus the closed shell $3s^2$ configuration of Ga^+ forms a weak complex with N consistent with the small bond energy observed for the cation. The estimated ionization potential of GaN at the MRSDCI level is 7.50 ± 0.5 eV, whereas at the CCSD(T)/aug-cc-pVXZ, X = T,Q levels it is 7.69 and 7.8 eV, aug-cc-pVTZ and aug-cc-pVQZ results, respectively. Performing a two point extrapolation we obtain IP(GaN) = 7.88 eV, which is 1.88 eV larger than the IP of Ga [32] and much lower than the IP of Nitrogen, 14.53 eV.

3.4. Dissociation energy

The dissociation energy of GaN was determined at the DKCCSD(T)/cc-pVTZ_DK and DKCCSD(T)/cc-pVQZ_DK levels as 41.51 and 44.56 kcal/mol, respectively. Therefore, after extrapolation to the complete basis set limit the obtained D_e is 46.79 kcal/mol. However, it is mandatory to include core and spin–orbit corrections. The core valence correlation contribution to the bond energy is 1.62 kcal/mol. To estimate the spin–orbit correction, we use the atomic Ga spin–orbit splitting, which is 661 cm^{-1}. Manna and Das [33] estimated the spin orbit splitting in

Table 4
Comparison between MRSDCI/[Ga(4s4p2d),N(4s4p1d)]+ECPs and MRSDCI/aug-cc-pVQZ[a] results

State	Method					
	ECP[b]	AQZ[a]	ECP[b]	AQZ[a]	ECP[b]	AQZ[a]
	T_e (cm^{-1})	T_e (cm^{-1})	r_e (Å)	r_e (Å)	ω_e (cm^{-1})	ω_e (cm^{-1})
$^3\Sigma^-$(I)	0.0	0.0	1.964	2.021	530	502
$^3\Pi$(I)	532	645	1.828	1.873	635	622
$^1\Sigma^+$(I)	6135	6452	1.691	1.751	816	780
$^1\Pi$(I)	8318	7340	1.789	1.830	699	735
$^1\Delta$(II)	12 343	10 969	1.950	1.994	559	514
$^1\Sigma^+$(II)	20 056	18 851	1.916	1.947	631	641
$^3\Sigma^+$(I)	21 197	20 810	1.686	1.735	774	744
$^3\Pi$(II)	26 013	23 794	1.807	1.883	642	552
$^3\Pi$(III)	26 337	29 037	2.099	2.12	326	447
$^1\Pi$(II)	30 768	27 908	1.943	1.973	614	499

[a] Results taken from Ref. [6]. Obtained at the MRSDCI/aug-cc-pVQZ level of theory.

[b] Results obtained at the MRSDCI level employing ECPs and a (4s4p2d) basis set on Ga and a (4s4p1d) basis set on N.

the $^3\Sigma^-$(I) ground state of isoelectronic GaP to be only 5 cm^{-1}. Because of the similar electronic configurations and bonding in GaN and GaP we can expect a similar splitting for the $^3\Sigma^-$ state of GaN. Our estimated D_e with all these corrections is 46.5 ± 1 kcal/mol.

3.5. Comparison with MRSDCI/aug-cc-pVQZ results

In Table 4, we have compared the MRSDCI/aug-cc-pVQZ results obtained by Uneo and co-workers [6] for the ground and nine excited states of GaN and our MRSDCI results by employing relativistic effective core potentials and 4s4p2d1f basis sets on Gallium and 4s4p1d basis sets on N. In the case of the transition energies the results obtained by both procedures are in good agreement for the $^3\Pi$ and $^1\Sigma^+$ states. However, for the higher excited states there are differences. For example, for the $^1\Pi$(II) state the deviation is close to 3000 cm^{-1}. In previous sections, we have shown that the small basis set and ECPs exhibit error cancellations compared to large basis sets with core correlations explicitly included. Therefore, it is not clear if the differences noted in Table 4 are due to lack of 3d-core correlation in the work of Uneo and co-workers [6].

4. Conclusions

The ground and low lying excited states of GaN has been investigated employing MRSDCI and coupled cluster methodologies. Both methodologies indicate that the ground state of GaN is $^3\Sigma^-$. At the MRSDCI level the $^3\Sigma^-$ state is 532 cm^{-1} below the $^3\Pi$ state, whereas at the DKCCSD(T)/CBS level the separation is 857 cm^{-1}. The splitting between the $^3\Sigma^-$ and $^3\Pi$ states was reduced to about 700 cm^{-1} by core correlation. Most of the low lying excited states undergo crossing with repulsive $^5\Sigma^-$ and $^5\Pi$ states causing predissociation. For GaN$^-$ the ground state is $^2\Sigma^+$, although there is a very low lying excited state $^2\Pi$, 662 cm^{-1}. The electron affinity of GaN is 1.44 ± 0.5 eV. The cation is a slightly bound Ga$^+$–N complex with an IP of 7.88 eV. The dissociation energy of GaN was computed as 46.5 ± 1 kcal/mol.

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