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An ab Initio Study of the Low-Lying Doublet States of Linear and T-Shaped Ga$\cdot$N$_2$

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The lowest-lying $^2\Pi$ and $^2\Sigma$ states (linear structure), and $^2A_1$, $^2B_1$, and $^2B_2$ states (T-shaped structure) of the Ga$\cdot$N$_2$ complex were studied by ab initio calculations. The B3LYP, MP2, QCISD, and CCSD(T) methods were employed with various all-electron and ECP basis sets to obtain reliable minimum-energy geometries and harmonic vibrational frequencies for these electronic states. The ground state was found to be the $\tilde{X}^2\Pi$ state; the other states considered were of ca. 300 cm^{-1} higher in energy. The interaction energy (including the full counterpoise correction for basis set superposition error and relativistic correction) of complex formation, ΔE_e(CP) (Ga$\cdot$N$_2$ $\tilde{X}^2\Pi$), was calculated to be −1.1 kcal.mol^{-1} (−400 cm^{-1}) at the RCCSD(T) level with basis sets of better than augmented-polarized-valence-quadruple-ζ quality. The best estimates of D_0 and enthalpy of formation at 298 K for the $\tilde{X}^2\Pi_{1/2,3/2}$ spin−orbit states are $D_0 = 95$, 320 cm^{-1} and $\Delta H^{298K} = 0.07$, −0.58 kcal.mole-1, respectively. Both spin−orbit components of the $\tilde{X}^2\Pi$ state of Ga$\cdot$N$_2$ are weakly bound at 0 K. The complex formation of the $\tilde{X}^2\Pi_{1/2}$ and $\tilde{X}^2\Pi_{3/2}$ states are slightly endothermic and exothermic, respectively, at room temperature.

Introduction

Recently, two spectroscopic studies on the interaction and/or reaction of a Ga atom with a N$_2$ molecule have appeared. They are a laser-induced fluorescence (LIF) spectroscopy study of the Ga$\cdot$N$_2$ complex by Ellis et al.[1] and an infrared matrix-isolation study on reactions of laser-ablated Group 13 (or III B) atoms with N atoms and molecules by Zhou and Andrews.[2] (On the general interest of semiconducting materials involving group III nitrides, and/or weakly bound complexes with an open-shell metal atom, see refs 1 and 2, and references therein.) In the LIF study,[1] two strong band systems were observed above 30 000 cm^{-1}, which were assigned to the $^2\Delta \leftarrow \tilde{X}^2\Pi_{3/2}$ and $^4\Sigma^- \leftarrow \tilde{X}^2\Pi$ transitions of Ga$\cdot$N$_2$. (The specific spin−orbit component of the $\tilde{X}^2\Pi$ state in the latter transition was uncertain.) Dispersed fluorescence spectra were also reported. However, all of the observed emissions in the dispersed spectra were assigned to Ga transitions and no emission from the complex was identified. Nevertheless, it was mentioned in ref 1 that the ground state of Ga$\cdot$N$_2$ has been shown to be linear by unpublished ab initio calculations[1] and by comparison with published ab initio calculations[3] on Al$\cdot$N$_2$. For the former calculations on Ga$\cdot$N$_2$ by Ellis et al.,[1] the details were not given in ref 1, but the T-shaped geometry was reported to be a transition state on the potential energy surface (the state symmetry of this transition state was not given). In QCISD(T) calculations on Al$\cdot$N$_2$ by Chaban and Gordon,[3] it seems that only the lowest-lying linear states, $^2\Pi$ and $^2\Sigma$, were considered.

In the infrared matrix-isolation study of Zhou and Andrews,[2] density functional (B3LYP/6-311+G*) calculations were also performed on various GaN$_2$ structures in order to assist spectral assignments.[2] Contrary to what was reported by Ellis et al.[1] on Ga$\cdot$N$_2$, the lowest doublet states of GaNN and Ga(N$_2$) (presumably with linear and T-shaped structures respectively) were found to dissociate by Zhou and Andrews in their density functional (DFT) calculations (convergence was obtained to Ga + N$_2$). In view of the results obtained from the DFT calculations of Zhou and Andrews,[2] and the nonobservance of Ga$\cdot$N$_2$ emission in the dispersed fluorescence spectra of Ellis et al.[1] mentioned above, it seems that it is not absolutely certain if Ga$\cdot$N$_2$ is bound in its ground electronic state.

With a ground electronic state configuration of ...4s^{2}4p^1 for Ga, and the possibility of the complex having a linear ($C_{\infty v}$) or T-shaped (C_{2v}) structure, five lowest-lying doublet electronic states, namely $^2\Pi$, $^2\Sigma$, $^2A_1$, $^2B_1$, and $^2B_2$, are possible candidates for the ground state of Ga$\cdot$N$_2$. From the evidence given above, it seems that a more thorough computational investigation is required to determine the ground-state structure of the Ga$\cdot$N$_2$ complex; spectroscopic assignments could then be made on a more reliably footing. Therefore, the first part of the present series of papers on Ga$\cdot$N$_2$ has been aimed at determining the ground electronic state of the complex and its minimum-energy geometry by performing high-level ab initio calculations on the above-mentioned five electronic states of Ga$\cdot$N$_2$. In addition, higher-level calculations were carried out for the ground state obtained, to determine accurately D_0 and ΔH^{298K} of Ga$\cdot$N$_2$ complex formation. Low-lying excited doublet and quartet states of Ga$\cdot$N$_2$ will be considered subsequently in order to confirm (or revise) the state assignments of the two band systems observed by Ellis et al.[1] These further studies will be reported in a forthcoming publication.[4]

Computational Details. Geometry optimization and harmonic frequency calculations were carried out for the lowest-lying $^2\Pi$, $^2\Sigma$, $^2A_1$, $^2B_1$, and $^2B_2$ states of Ga$\cdot$N$_2$ at the B3LYP, MP2, QCISD, and CCSD(T) levels with various standard basis sets. Unrestricted-spin Hartree−Fock (UHF) wave functions were employed for all these doublet states, unless otherwise stated. Nevertheless, the computed $\langle S^2 \rangle$ values are <0.765 in all cases, suggesting negligibly small spin-contamination. For the MP2, QCISD, and CCSD(T) calculations, the frozen core approximation was applied, unless otherwise stated.

For the ground state obtained ($^2\Pi$; see next section), further geometry optimization and harmonic frequency calculations were carried out, including calculations employing the lanl2, Los Alamos effective core potential[5] (ECP), coupled with three

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different augmented valence Gaussian basis sets, namely lanl2-[8s7p4d], lanl2[8s6p5d] and lanl2[8s6p5d2f], for Ga. (The corresponding basis sets employed for N are 6-311+G(3d) for the first two Ga ECP basis sets, and 6-311+G(3df) for the last.) The [8s7p4d] contraction for Ga 4s and 4p valence shells has the first s and p contractions from 8s (largest exponent, 1.6; ratio, 1.8) and 7p (1.2, 2.0) primitives, respectively, with their contraction coefficients obtained from an atomic ROHF calculation, employing the primitives uncontracted. The rest of the contraction consists of uncontracted 7s (largest exponent, 1.2; ratio, 2.5), 6p (0.4, 2.5) and 4d (0.7, 3.0) functions. Similarly, the [8s6p5d] contraction has the first s and p contractions from 12s (largest exponent, 1.5; ratio, 1.5) and 7p (1.2, 2.0) primitives and the rest, uncontracted 7s (0.8, 3.0), 5p (0.3, 3.2) and 5d (0.3, 3.0) functions. For the [8s6p5d2f] contraction, the s, p, and d parts are the same as in the [8s6p5d] contraction; the uncontracted 2f functions have the exponents 0.2 and 0.04.

In addition, some calculations, which include some core electrons in the correlation treatment, were also carried out in order to assess the effect of core correlation on the optimized geometry. All these calculations were performed with the Gaussian94/98[6] suite of programs.

To calculate reliably the interaction energy (ΔE_e) for complex formation, the RCCSD(T) method[7] in the MOLPRO[8] suite of programs was employed. Basis set superposition error (BSSE) was corrected by the full counterpoise (CP) method.[9] The optimized geometry of the ground-state complex obtained at the CCSD(T)/6-311+G(3df) level was used in the calculation of the interaction energy. Two all-electron basis sets, AQZ-1 and AQZ-2, and a very high quality effective core potential basis set, ECP[11s10p6d5f3g], were employed for Ga in these RCCSD(T) calculations. The corresponding basis set for *N* is the standard aug-cc-pVQZ basis set in all cases.

There are two reasons for designing the two all-electron basis sets, AQZ-1 and AQZ-2. First, the standard aug-cc-pVQZ basis set[8,10] of Ga was found to be inadequate for calculating the interaction energy of the Ga•N$_2$ complex, giving a large positive ΔE_e(CP) (i.e., highly unbound), contrary to the results obtained using the ECP[11s10p6d5f3g] basis set and the newly designed AQZ-1 and AQZ-2 basis sets (see later text and next section). It should be noted that the d functions in the Ga basis set have two different purposes, namely, accounting for the 3d occupied orbitals and also serving as polarization functions for the valence electrons. The uncontracted d functions in the standard aug-cc-pVQZ basis set appear to be too diffuse as polarization functions in the complex calculation (see also later text). Second, to examine the core correlation effect on the computed interaction energy, the standard aug-cc-pVQZ basis set was expanded in the core region so as to allow proper inclusion of some core electrons in the correlation calculation.

The AQZ-1 basis set for Ga is expanded from the standard aug-cc-pVQZ basis set in the following way. The three most diffuse d primitives in the contracted d set are uncontracted. That is, the original d contraction of [9,1,1,1,1] is now changed to [6,1,1,1,1,1,1,1]. This uncontraction of the d orbital space is required, because the original d contractions, which appear to be designed essentially for the 3d occupied orbital of Ga, have the uncontracted d functions being too diffuse to serve as polarization functions for the valence electrons. With the above expansion of the d orbital space, the AQZ-1 basis is also suitable to be used in correlation calculations, which include the 3d electrons in the correlation treatment. The AQZ-2 basis set is an expansion based on the AQZ-1 basis set, so as to make it suitable for the $3s^23p^63d^{10}$ electrons to be correlated in the RCCSD(T) calculations (i.e., only the $1s^22s^22p^6$ electrons of Ga are frozen). The following uncontracted functions (exponents) are augmented to the AQZ-1 basis set: s, 2.319016, 0.773022; p, 3.536447, 0.9823464; f, 2.0; g, 1.7. The total numbers of contracted basis functions in the complex calculations, with the aug-cc-pVQZ, AQZ-1 and AQZ-2 basis sets for Ga (and the aug-cc-pVQZ basis set for N), are 253, 268, and 292, respectively.

TABLE 1: Optimized Geometrical Parameters and Computed Harmonic Frequencies (cm^{-1}) of the Lowest $^2A_1$ State of Ga•N$_2$ (T-Shape)

method	GaN/Å	NN/Å	NGaN/deg	a_1	a_1	b_2
MP2/6-311+G(2d)	5.0934	1.1060	12.5	2230.6	17.8	79.1
QCISD/6-311+G(2d)	5.1932	1.0933	12.1	2415.8	16.2	18.0
CCSD(T)/6-311+G(2d)[a]	5.3481	1.0980	11.8			
CCSD(T)/6-311+G(3df)[a]	5.3479	1.0973	11.8			

[a] SCF convergence failure in the numerical second derivative calculation.

The ECP[11s10p6d5f3g] basis set for Ga employs the quasi-relativistic effective core potential of Stuttgart[8] (ECP28MWB). The corresponding valence contracted basis set has the first s, p and d contractions of 15s (largest exponent, 7.0; ratio, 2.0), 11p (2.5; 2.0) and 5d (0.25; 3.0) primitives, respectively. The contraction coefficients for the s and p contracted functions were obtained from an atomic ROHF calculation, while for the d contracted set, the contraction coefficients were obtained from the ROHF calculation on the $^2\Delta$ state of the Ga•N$_2$ complex.[4] The rest of the contraction consists of the following uncontracted functions: 10s (largest exponent, 2.75; ratio, 2.4), 9p (1.8, 2.5), 5d (0.15, 3.0), 5f (0.15, 3.0) and 3g (0.144, 4.0). There are two purposes of employing such an ECP basis set. First, with the ECP28MWB ECP, there are only three valence electrons for Ga to be considered. The augmented-polarized-valence basis set designed here should have saturated the valence and intermolecular region. Second, some relativistic contribution would be included by use of the quasi-relativistic ECP.

Spin−orbit (SO) interaction in the ground states of Ga•N$_2$ and Ga were considered by employing the full Breit−Pauli SO-operator, with the CASSCF wave functions of the lowest lying $^2\Pi$ and $^2\Sigma$ states of the complex, and the ^2P state (p_x^1, p_y^1, and p_z^1 configurations) of the Ga atom. The (20s15p9d) uncontracted Gaussian basis set of Partridge[8,11] and the uncontracted aug-cc-pVDZ basis set were used for Ga and N, respectively, in these calculations. The active space in the CASSCF calculation includes all valence orbitals. The full SO matrix for the electronic states considered was diagonalized and the SO splittings were obtained using the MOLPRO[8] suite of programs. The energy lowering of the lower component of the spin−orbit split $^2\Pi$ state ($^2\Pi_{1/2}$) of the complex and the ^2P state ($^2P_{1/2}$) of Ga from the corresponding unsplit levels were used together with the RCCSD(T) energies to give the interaction energy of complex formation of the $\tilde{X}^2\Pi_{1/2}$ state of Ga•N$_2$ (see next section).

Thermodynamic quantities, $\Delta H^{\varnothing}$, $\Delta S^{\varnothing}$, and $\Delta G^{\varnothing}$, for the complex formation were calculated within the rigid-rotor harmonic-oscillator (RRHO) model.

Results and Discussion

The results of the calculations are summarized in Tables 1−7. The optimized geometrical parameters and computed harmonic vibrational frequencies of the five lowest-lying electronic states of Ga•N$_2$ obtained at different levels of theory are given in Tables 1−5. The computed relative electronic energies of these states are compared in Table 6. From this table it is clear that

TABLE 2: Optimized Geometrical Parameters and Computed Harmonic Frequencies (cm^{-1}) of the Lowest $^2B_1$ State of Ga·N$_2$ (T-Shape)

method	GaN/Å	NN/Å	NGaN/deg	a_1	a_1	b_2
MP2/6-311+G(2d)	4.0295	1.1062	15.8	2228.3	28.3	43.7i
QCISD/6-311+G(2d)	4.2136	1.0934	14.9	2414.5	22.6	35.6i
CCSD(T)/6-311+G(2d)[a]	4.1180	1.1016	15.4			
CCSD(T)/6-311+G(3df)	4.2270	1.0975	14.9	2379.0	16.0	35.0i

[a] Not optimized geometry; optimization procedure unable to determine next point.

TABLE 3: Optimized Geometrical Parameters and Computed Harmonic Frequencies (cm^{-1}) of the Lowest $^2B_2$ State of Ga·N$_2$ (T-Shape)

method	GaN/Å	NN/Å	NGaN/deg	a_1	a_1	b_2
B3LYP/6-31G*	2.7262	1.1247	23.8	2184.5	44.9	187.1
B3LYP/6-311+G*	3.3214	1.1004	19.1	2353.9	36.2	104.2
B3LYP/6-311+G(2d)	3.2634	1.0969	19.4	2336.6	35.6	114.3
B3LYP/6-311+G(3df)	3.2914	1.0961	19.2	2355.5	28.3	109.8
MP2/6-311+G(2d)	3.9677	1.1066	16.0	2225.0	26.9	28.8i
QCISD/6-311+G(2d)	4.1917	1.0935	15.0	2413.6	20.6	39.4i
CCSD(T)/6-311+G(2d)[a]	4.0280	1.0984	15.7			
CCSD(T)/6-311+G(3df)[a]	4.0102	1.0978	15.7			

[a] SCF convergence failure in the numerical second derivative calculation.

TABLE 4: Optimized Geometrical Parameters (angstroms) and Computed Harmonic Vibrational Frequencies (cm^{-1}) of the Lowest $^2\Sigma$ State of Linear Ga·N$_2$

method	GaN	NN	σ	σ	π
MP2/6-311+G(2d)	5.3875	1.1061	2229.8	11.6	20.3
QCISD/6-311+G(2d)	5.4575	1.0934	2414.6	10.8	7.5
CCSD(T)/6-311+G(2d)[a]	5.3512	1.0981			
CCSD(T)/6-311+G(3df)[a]	5.6813	1.0974			

[a] SCF convergence failure in the numerical second derivative calculation.

TABLE 5: Optimized Geometrical Parameters (angstroms) and Computed Harmonic Vibrational Frequencies (cm^{-1}) of the $\tilde{X}^2\Pi$ State of Linear Ga·N$_2$

method	GaN	NN	σ	σ	π
B3LYP/6-31G*	2.2548	1.1247	2133.3	154.7	162.7;216.6
B3LYP/6-311+G*	2.6977	1.1026	2289.8	45.8	45.5;76.1
B3LYP/6-311+G(2d)	2.8665	1.0955	2336.8	41.7	57.6;79.2
B3LYP/6-311+G(3df)	2.8004	1.0959	2333.3	39.1	64.9;91.4
MP2/6-31G*	3.2048	1.1187	2416.0	71.8	71.0;75.0
MP2/6-311+G(2d)	3.3946	1.1060	2242.2	44.2	45.0;49.0
MP2(full)/6-311+G(2d)	3.2664	1.1124	2248.5	52.7	70.3;72.7
MP2/6-311+G(3df)	3.2576	1.1051	2267.0	53.5	54.4;57.9
QCISD/6-311+G(2d)	3.5529	1.0932	2416.6	36.5	45.1;48.3
CCSD(T)/6-311+G(2d)	3.4625	1.0979	2365.5	40.1	39.5;48.5
CCSD(T)/6-311+G(3df)	3.2905	1.0973	2380.6	49.8	56.9;58.5
CCSD{T,FC (2p)}/6-311+G(3df)[a]	3.1356	1.1034	-		
QCISD/lanl2 [8s7p4d],6-311+G(3d)	3.4865	1.0999	2381.5	38.1	47.3;47.4
QCISD/lanl2 [8s6p5d],6-311+G(3d)	3.4865	1.0999	2381.6	39.4	48.6;48.9
CCSD(T)/lanl2 [8s6p5d2f],6-311+G(3df)	3.2921	1.1034	2342.2	50.0	58.1;69.1

[a] The frozen core includes N 1s^2 and Ga 1s^{2}2s^{2}2p^6; Ga 3s^{2}3p^{6}3d^{10} electrons are included in the correlation treatment; harmonic vibrational frequency calculation has not been carried out because of the anticipated extremely demanding computational resources required.

TABLE 6: Relative Total Electronic Energies of the Various Low-Lying Electronic States of Ga·N$_2$

E_{rel}/kcal mol^{-1} (cm^{-1})	$\tilde{X}^2\Pi$	$^2B_1$	$^2B_2$	$^2A_1$	$^2\Sigma$
B3LYP/6-311+G(2d)	0.0		0.95 (333)		
B3LYP/6-311+G(3df)	0.0		1.10 (348)		
MP2/6-311+G(2d)	0.0	0.76 (264)	0.82 (287)	0.94 (327)	1.11 (389)
QCISD/6-311+G(2d)	0.0	0.57 (206)	0.65 (228)	0.68 (237)	0.82 (288)
CCSD(T)/6-311+G(2d)	0.0	0.65 (226)[a]	0.72 (250)	0.79 (277)	0.94 (328)
CCSD(T)/6-311+G(3df)	0.0	0.88 (306)	0.89 (312)	1.01 (353)	1.19 (417)

[a] Not optimized geometry; see footnote a of Table 2.

the ground state has a linear $C_{\infty v}$ structure and is the $\tilde{X}^2\Pi$ state. However, the low-lying excited states considered are only a few hundred wavenumbers above the ground state. In contrast to Al·N$_2$, where the lowest $^2\Sigma$ state was found to be entirely repulsive,[3] the lowest $^2\Sigma$ state of Ga·N$_2$ seems to be just bound (without correction for basis set superposition error (BSSE) and spin−orbit interaction), with a very long intermolecular bond length (>5.0 Å) and also with very low intermolecular vibrational frequencies (Table 4; see also later text). For the three lowest doublet states of T-shaped structures, two of them ($^2B_1$ and $^2B_2$) seem to be saddle points, each with one imaginary frequency of b_2 symmetry (asymmetric stretch, which would probably lead to a linear structure). Only the $^2A_1$ state is a true minimum.

Regarding the DFT results reported by Zhou and Andrews,[2] we repeated the B3LYP/6-311+G* calculations on both linear and T-shaped Ga·N$_2$. Contrary to their findings, we obtained optimized geometries and all real vibrational frequencies, as shown in Tables 3 and 5. B3LYP calculations with different basis sets carried out in the present study gave true minima for both linear and T-shaped Ga·N$_2$ complexes in all cases (Tables 3 and 5). Therefore, it seems conclusive that the B3LYP method does give bound Ga·N$_2$ complexes (though weakly bound, as will be discussed later). However, the DFT results have also their own problems, which are discussed below.

For the T-shaped structure, the B3LYP optimizations gave the $^2B_2$ state as a true minimum (see Table 3). However, both the MP2 and QCISD calculations gave one imaginary frequency for the $^2B_2$ state. In addition, for both the $^2B_2$ and the $^2\Pi$ states, the computed DFT intermolecular bond lengths (GaN) (Tables 3 and 5) were found to be significantly shorter than those obtained with the MP2, QCISD, and CCSD(T) methods, particularly when relatively smaller basis sets were used. The DFT GaN bond lengths are also rather sensitive to the basis sets used. In view of these considerations, it also seems conclusive that the B3LYP method is inadequate for this type of complex and the DFT results should be viewed with caution.

From here onward, we will only consider the $\tilde{X}^2\Pi$ state of Ga·N$_2$, and concentrate on the ab initio results, ignoring the DFT results. Considering the intermolecular GaN bond length, the computed values are rather sensitive to the levels of calculations used to obtain them (Table 5). The MP2 values increase and then decrease when the basis sets are increased in size and/or quality. The 6-311+G(2d) basis set gave a relatively large GaN bond length with all the correlation methods employed, suggesting that even a split-valence triple-ζ plus diffuse and double polarization basis set is inadequate to obtain a reliable geometry of the Ga·N$_2$ complex. Nevertheless, the ECP basis sets designed here with the lanl2 ECP seem to be performing very well, giving results almost identical to the all-electron basis sets of similar valence quality. However, all QCISD intermolecular bond lengths are relatively large, suggesting that the triple excitations are particularly important for obtaining a reliable intermolecular bond length for this type of complex. In general, it seems that calculations with a larger basis set and/or at a higher level of correlation result in a shorter GaN bond length. At the highest levels of geometry optimization carried out in this work, the CCSD(T) calculations with the 6-311+G(3df) and lanl2[8s6p5d2f] basis sets, the computed

TABLE 7: Computed Interaction Energies (ΔE_e) and Thermodynamic Quantities (in kcal mol^{-1} (cm^{-1}), unless Stated Otherwise) of the Ga•N_2 ($\tilde{X}^2\Pi$) Complex Formation at the RCCSD(T) Level[a]

Ga•N_2 $\tilde{X}^2\Pi$	ECP-[11s10p6d5f3g]	FC/AQZ-1[b]	FC(3p)/AQZ-1[b]	FC(2p)/AQZ-2[b]
ΔE_e	−1.26 (−440.2)	−1.03 (−360.9)	−1.27 (−444.2)	−1.28 (−447.6)
BSSE(Ga)	(51.1)	(6.3)	(57.7)	(50.2)
BSSE(N_2)	(24.6)	(19.8)	(19.8)	(20.1)
$\mathrm{BSSE}_{\mathrm{total}}$	(75.7)	(26.1)	(77.5)	(70.3)
ΔE_e(CP)	−1.04 (−364.5)	−0.96 (−334.8)	−1.05 (−366.7)	−1.08 (−377.3)
ΔE_{rel}	(−22)			
ΔSO($\tilde{X}^2\Pi_{1/2}$)[c]	(211.4)			
ΔSO($\tilde{X}^2\Pi_{3/2}$)[c]	(−1.0)			
D_e($\tilde{X}^2\Pi_{1/2}$)	(175.1)	(145.4)	(177.3)	(187.9)
D_e($\tilde{X}^2\Pi_{3/2}$)	(387.5)	(357.8)	(389.7)	(400.3)
Δ(ZPVE)[d]	0.27 (93.4)			
D_0($\tilde{X}^2\Pi_{1/2}$)	(81.7)	(52.0)	(83.9)	(94.5)
D_0($\tilde{X}^2\Pi_{3/2}$)	(294.1)	(284.4)	(296.3)	(306.9)
$\Delta E_{\mathrm{thermal}}$(298K)[e]	0.34 (118.2)			
ΔH^{298}($\tilde{X}^2\Pi_{1/2}$)	0.10 (36.5)	0.18 (66.2)	0.10 (34.3)	0.07 (23.7)
ΔH^{298}($\tilde{X}^2\Pi_{3/2}$)	−0.50 (175.9)	−0.48 (166.2)	−0.51 (178.1)	−0.54 (188.7)
ΔS^f/cal mol^{-1} K^{-1}	−12.6			
ΔG^{298}($\tilde{X}^2\Pi_{1/2}$)	3.85	3.93	3.85	3.82

[a] At the UCCSD(T)/6-311+G(3df) geometry of the Ga•N_2 ($\tilde{X}^2\Pi$) complex; negative signs for ΔE_e and ΔE_e(CP), and positive signs for D_e and D_0, mean that the complex is bound. [b] AQZ-1 and AQZ-2 are extended aug-cc-pVQZ basis sets for Ga (see text for details); FC denotes frozen core: N 1s kept frozen in the RCCSD(T) treatment throughout (including the ECP basis calculation); for Ga, the frozen cores are from 1s to 3d (normal default: $1s^22s^22p^63s^23p^63d^{10}$), 3p and 2p, respectively. [c] Spin−orbit splitting correction (see text). [d] The zero-point vibrational energies for both spin−orbit states of Ga•N_2 are assumed to be the same from the UCCSD(T)/6-311+G(3df) vibrational frequency calculations. [e] At 298 K, including rotational, translational, vibrational and *nRT* terms, assuming a rigid motor harmonic oscillator model; vibrational frequencies from UCCSD(T)/6-311+G(3df) calculations. [f] Experimental value for N_2, from CODATA;[13] UCCSD(T)/6-311+G(3df) values for the complex.

GaN bond lengths agree very well. The best estimate of the intermolecular bond length for the $\tilde{X}^2\Pi$ state of Ga•N_2, based on the highest level calculations is 3.29 Å from the present study.

However, the effect of basis set superposition error (BSSE) has not been considered explicitly in obtaining the optimized geometry. Correcting for BSSE would be expected to give a longer intermolecular bond length. However, including some core electrons in the correlation treatment, the MP2(full)/6-311+G(2d) and CCSD{T,FC(2p)}/6-311+G(3df) geometry optimization calculations (see Table 5; it is also noted that the latter geometry optimization was very demanding in terms of computing time) gave shorter GaN bond lengths, when compared with those obtained from the corresponding frozen core calculations. In view of these opposite effects on the intermolecular bond length, the present best estimate should be reasonably reliable, at least for the purpose of calculating the interaction energy of complex formation (see also later text).

Considering the computed harmonic vibrational frequencies, in general, trends similar to those discussed above on the computed intermolecular geometrical parameters can be observed (Table 5). However, the computed harmonic vibrational frequencies seem to be significantly less sensitive to the levels of calculation used to obtain them than the computed GaN bond lengths. The consistency in the computed vibrational frequencies suggests that they should be reasonably reliable.

The computed interaction energies ΔE_e, obtained at different levels of calculations, are shown in Table 7 (a negative sign for ΔE_e means that the complex is bound). It is encouraging that the computed results obtained with the ECP[11s10p6d5f3g] and all-electron basis sets are close to each other (all the computed ΔE_e(CP) values are within 43 cm^{-1}). For the calculations employing the all-electron basis sets, AQZ-1 and AQZ-2, although the computed ΔE_e values, without CP correction for BSSE, become more negative with a larger basis set and/or more core electrons being included in the correlation treatment, the changes in the CP corrected values, ΔE_e(CP), with the levels of calculation, are significantly smaller than the CP uncorrected ones. It is clear that a large portion of gain in the interaction energy is due to BSSE. After correcting for BSSE, the difference between the CP corrected interaction energy, ΔE_e(CP), obtained at the RCCSD{T,FC(3p)}/AQZ-1 and RCCSD{T,FC(2p)}/AQZ-2 levels of calculation are only ca. 10 cm^{-1}. From the results given in Table 7, it can be concluded that the ΔE_e(CP) value is not expected to change significantly with any further enlargement of the basis set and/or inclusion of more core electrons in the correlation treatment.

Relativistic correction to the interaction energy for the Ga•N_2 complex formation ΔE_{rel} has also been calculated using MOLPRO by computing the expectation values of the mass−velocity and one-electron Darwin terms[8] at the RHF level with different basis sets. ΔE_{rel} was evaluated as the difference of the relativistic contributions between the complex and the monomers. In the spirit of the full CP correction,[9] the calculations of the relativistic contributions for the monomers have employed the full basis set of the complex at the CCSD(T)/6-311+G(3df) geometry of the latter. The values of ΔE_{rel} obtained with the aug-cc-pVTZ (with no f functions), aug-cc-pVTZ, uncontracted aug-cc-pVTZ and AQZ-2 basis sets are −21.1, −22.0, −27.6, and −18.1 cm^{-1}, respectively. On the basis of these calculations, the best estimate for ΔE_{rel} would be ca. −22 ± 5 cm^{-1}. With ΔE_e(CP) calculated to be −377 cm^{-1} at the highest level of RCCSD{FC(2p),T}/AQZ-2 (Table 7), the best estimate of $\Delta \mathrm{E}_e$(CP), including relativistic correction, from this study, is therefore −1.1 kcal mol^{-1} (−400 cm^{-1}).

We also note that ΔE_e(CP) was evaluated with the CCSD{T,FC(2p)}/6-311+G(3df) geometry (see Table 5) at the RCCSD(T)/ECP[11s10p6d5f3g] and RCCSD{T,FC(2p)}/AQZ-2 levels of calculation, giving values of −0.97 (−339.2) and −1.06 (−369.9) kcal mol^{-1} (cm^{-1}), respectively. Both these values were obtained at a slightly shorter intermolecular distance (due to the inclusion of some core electrons in the correlation treatment in the geometry optimization calculation) and are very slightly less negative than the corresponding values obtained with the CCSD(T)/6-311+G(3df) geometry (only the valence electrons were considered) given in Table 7. Although we have not produced a CP corrected intermolecular surface, these CP corrected ΔE_e(CP) calculations favor the CCSD(T)/6-311+G(3df) geometry as the minimum, and support the expectation given above that the gain in the electronic energy with the core electrons being included in the correlation treatment is largely canceled by the correction of BSSE. In any case, comparing these ΔE_e(CP) values obtained at two different intermolecular distances, it can be concluded that the intermolecular surface is very flat and the geometry effect on ΔE_e(CP) is expected to be small.

Before correction for spin−orbit (SO) splittings in the evaluation of interaction energy is discussed, it should be noted that CASSCF and SO calculations were also performed at the long intermolecular distance of GaN = 30.0 Å. These calculations are for the purpose of establishing the correlation of the SO states, $^2\Pi_{1/2}$, $^2\Pi_{3/2}$, and $^2\Sigma_{1/2}$, of the complex with the $^2P_{1/2}$ and $^2P_{3/2}$ states of the Ga atom at the dissociation limits. The correlation of the $^2\Pi_{3/2}$ state of the complex with the $^2P_{3/2}$ state of Ga is unambiguous. From the CASSCF/SO calculations at the above-mentioned long intermolecular distance, the $^2\Pi_{1/2}$ state of the complex was found to correlate with the $^2P_{1/2}$ Ga atomic limit, while the $^2\Sigma_{1/2}$ state correlates with the $^2P_{3/2}$ atomic limit. The energies of the $^2\Pi_{3/2}$ and $^2\Sigma_{1/2}$ states relative to the $^2\Pi_{1/2}$ state at GaN = 30.0 Å were calculated to be 812.8 and 757.3 cm^{-1}, respectively, which compare well with the computed SO splitting of 778 cm^{-1} for atomic Ga (see later text). The unperturbed $^2\Pi$ level was computed to be 81.4 cm^{-1} above the $^2\Sigma$ level by CASSCF calculations at this long GaN distance. However, the unperturbed $^2\Sigma$ level has to be more than 260 cm^{-1} lower in energy than the $^2\Pi$ level, in order for the $^2\Sigma_{1/2}$ SO state to correlate with the $^2P_{1/2}$ atomic limit. This is because first-order SO splitting between the $^2\Pi_{3/2,1/2}$ states was calculated to be 521.8 cm^{-1} at this long intermolecular distance (i.e., the $^2\Pi_{1/2}$ state is 260.9 cm^{-1} below the $^2\Pi$ level). We also note that, since the $^2\Sigma_{1/2}$ state of the complex correlates with the $^2P_{3/2}$ state of Ga, SO interaction would almost certainly increase the binding energy of the $^2\Sigma$ state (i.e., $^2\Sigma_{1/2}$ with respect to $^2P_{3/2}$ would be more bound than $^2\Sigma$ with respect to ^2P). This is because the SO effect at the atomic limit (where the $^2\Sigma-^2\Pi$ separation is small) is expected to be significantly larger than that at the equilibrium geometry of the complex (where the $^2\Sigma-^2\Pi$ separation is larger).

The spin−orbit (SO) splittings for the $\tilde{X}^2\Pi_{1/2,3/2}$ states of Ga·N$_2$ (at the CCSD(T)/6-311+G(3df) geometry) and the $\tilde{X}^2P_{1/2,3/2}$ states of Ga atom were calculated to be 565.6 and 778.0 cm^{-1} respectively. The latter value can be compared to the available experimental value[12] of 827 cm^{-1}. The computed value is smaller than the experimental value by 49 cm^{-1}, which is ca. 6% of the experimental value. The energy lowering of the $^2\Pi_{1/2}$ state of Ga·N$_2$ from the unperturbed $^2\Pi$ level is 307.3 cm^{-1}, and that of the $^2P_{1/2}$ state of Ga from the unperturbed ^2P level is 518.7 cm^{-1}. The correction to the interaction energy for SO splittings (ΔSO) in the complex and Ga atom is therefore +211.4 cm^{-1} for the $^2\Pi_{1/2}$ state of Ga·N$_2$ (a positive sign here means a reduction in the binding energy; see Table 7). In a similar way, the ΔSO correction for the $^2\Pi_{3/2}$ state has been evaluated to be −1.0 cm^{-1}. The D_e values obtained at the highest-level of calculations for the $X^2\Pi_{1/2,3/2}$ states are then 187.6 and 400.3 cm^{-1}, respectively [see Table 7; a positive D_e (or D_0) means that the complex is bound]. This is assuming that the shapes of the intermolecular energy surfaces of the two spin−orbit states are similar to that of the unperturbed $^2\Pi$ surface near their equilibrium positions; hence they have similar equilibrium geometries. This assumption seems reasonable, as consideration on the computed ΔE_e(CP) values obtained at different intermolecular distances for the unperturbed $^2\Pi$ surface given above suggests a very flat intermolecular energy surface near its equilibrium position. In addition, the effect of ΔSO correction on the $\tilde{X}^2\Pi_{3/2}$ intermolecular surface is monotonic, while that on the $\tilde{X}^2\Pi_{1/2}$ surface causes it to be more flat when compared with the unperturbed $^2\Pi$ surface. Moreover, the $\tilde{A}^2\Sigma_{1/2}$ state is significantly higher in energy than the $\tilde{X}^2\Pi_{1/2}$ state at the computed $\tilde{X}^2\Pi$ equilibrium geometry (>2900 cm^{-1} from the CASSCF/SO calculations); hence no avoided crossing between the two $\Omega = {}^1/_2$ SO states near their equilibrium positions would be expected. Summing up, employing the computed equilibrium geometry and harmonic vibrational frequencies {for zero-point-energy correction, Δ(ZPE)} of the unperturbed $^2\Pi$ state in the calculation of interaction energy and thermodynamic constants of the two SO split states, are reasonable approximations.

Combining ΔE_e(CP), ΔE_{rel}, ΔSO, and zero-point-energy correction, Δ(ZPE), the computed D_0, and other thermodynamic quantities for the complex formation, are summarized in Table 7. From the highest-level calculations performed in the present study, the $\tilde{X}^2\Pi_{1/2,3/2}$ states of Ga·N$_2$ are bound at 0 K (ie. D_0) by 95 and 307 cm^{-1} respectively. However, complex formation of the $\tilde{X}^2\Pi_{1/2}$ state at room temperature is slightly endothermic {ΔH^{298K} (Ga·N$_2$ $\tilde{X}^2\Pi_{1/2}$) = 0.07 kcal mol^{-1}}, though complex formation of the $\tilde{X}^2\Pi_{3/2}$ state is slightly exothermic (ΔH^{298K} (Ga·N$_2$ $\tilde{X}^2\Pi_{3/2}$) = −0.54 kcal mol^{-1}).

Concluding Remarks

High-level ab initio calculations have been carried out on the low-lying electronic states of the Ga·N$_2$ complex. On the basis of the computed results, it is concluded that the ground state has a linear structure and is the $\tilde{X}^2\Pi_{1/2}$ state. It is also established that the $\tilde{X}^2\Pi_{1/2}$ state correlates with the $^2P_{1/2}$ atomic limit of Ga, and the complex is weakly bound with the best-estimated $D_0(\tilde{X}^2\Pi_{1/2})$ value of ca.95 cm^{-1}. However, complex formation of this SO state is slightly endothermic at room temperature. Nevertheless, the higher SO state, the $\tilde{X}^2\Pi_{3/2}$ state is more well bound, with the best-estimated $D_0(\tilde{X}^2\Pi_{3/2})$ value of ca. 320 cm^{-1}. The uncertainty associated with the best-estimated ΔE_e(CP) value is expected to be less than −10 cm^{-1} (the negative sign means that the uncertainty is toward a larger binding energy), based on the results obtained from different levels of calculation carried out in this work. The uncertainty in ΔE_{rel} has been estimated above to be ±5 cm^{-1}. The uncertainties associated with the Δ(SO) values are estimated to be less than +13 and −0.5 cm^{-1} for the $\tilde{X}^2\Pi_{1/2}$ and $\tilde{X}^2\Pi_{3/2}$ states, respectively, assuming that the computed SO splittings are ca. 6% too small, based on the comparison between the computed and observed SO splittings in Ga atom. It can be seen that these uncertainties in ΔE_e(CP) and Δ(SO) roughly cancel each other for the $\tilde{X}^2\Pi_{1/2}$ state of the complex, and the above best-estimated D_0 values have taken these uncertainties into account.

The major uncertainties in D_0 and the thermodynamic constants obtained, which have not been considered in the present study, come from the RRHO approximation. However, going beyond the RRHO approximation would require scanning the intermolecular energy surface and then calculating the rovibrational energy levels from the surface, which is beyond the scope of the present study. With this approximation, however, the best estimates for ΔH^{298} of complex formation, based on the best-estimated D_0 values given above, are 0.07 and −0.58 kcal.mol^{-1} for the $\tilde{X}^2\Pi_{1/2}$ and $\tilde{X}^2\Pi_{3/2}$ states, respectively.

Referring to the LIF study of Ellis et al.,[1] the LIF band observed with an onset at 33468 cm^{-1} was assigned to the $^2\Delta$

$\leftarrow \tilde{X}^2\Pi_{3/2}$ transition. The reasoning given in ref 1 for assigning the initial state of this transition to the higher $\tilde{X}^2\Pi_{3/2}$ SO state rather than the lower $\tilde{X}^2\Pi_{1/2}$ SO state is summarized as follows. Assuming that $D_0(\tilde{X}^2\Pi_{1/2})$ is much smaller than $D_0(\tilde{X}^2\Pi_{3/2})$ and that the $^2\Delta$ state is more bound than the ground state, the geometry change in the $^2\Delta \leftarrow \tilde{X}^2\Pi_{1/2}$ transition would be expected to be larger than that in the $^2\Delta \leftarrow \tilde{X}^2\Pi_{3/2}$ transition. (This conclusion is based on the expected trend that, when D_0 increases, the intermolecular Ga−N bond length decreases.) Consequently, Franck−Condon (FC) factors of the $^2\Delta \leftarrow \tilde{X}^2\Pi_{3/2}$ transition would be expected to be more diagonal than those of the $^2\Delta \leftarrow \tilde{X}^2\Pi_{1/2}$ transition. The present study has yielded reliable computed D_0 values for the $\tilde{X}^2\Pi_{1/2,3/2}$ states of Ga•N_2, which were only speculative in the study of Ellis et al.[1] The computed D_0 values obtained here support the assumption made by Ellis et al.[1] on the relative magnitudes of D_0 for these two SO states. The equilibrium geometries of the $\tilde{X}^2\Pi_{1/2,3/2}$ SO states have not been obtained directly in the present study. Nevertheless, the minimum of the $\tilde{X}^2\Pi_{3/2}$ state is expected to coincide with that of the unperturbed $^2\Pi$ level. SO coupling between the $\tilde{X}^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ state would probably push the minimum of the $^2\Pi_{1/2}$ state to a slightly larger intermolecular bond length than that of the $\tilde{X}^2\Pi_{3/2}$ state. This is because the minimum of the $^2\Sigma$ level is at a larger intermolecular bond length than that of the $^2\Pi$ level. The $^2\Sigma-{}^2\Pi$ separation decreases and hence the SO interaction between the two $\Omega = {}^1/_2$ states increases, as the intermolecular distance increases from the minimum of the $^2\Pi$ level to the minimum of the $^2\Sigma$ level. In general, the present results on the computed thermodynamic constants of the two SO states support the preference of the $\tilde{X}^2\Pi_{3/2}$ state over the $\tilde{X}^2\Pi_{1/2}$ state in the assignment of the initial state of the LIF band at 33468 cm^{-1} suggested by Ellis et al.[1]

Regarding the assignments of the upper states of the two LIF bands, preliminary calculations on the lowest-lying $^2\Delta$ state and some low-lying quartet states of Ga•N_2 suggest that the assignment of the first LIF band system at 33468 cm^{-1} by Ellis et al.[1] is probably correct. However, the assignment of the second band system at 37633 cm^{-1} to the $^4\Sigma \leftarrow X^2\Pi$ transition is uncertain. Further calculations and spectral simulations are underway in order to firmly assign the LIF spectra. In addition, from preliminary calculations on some low-lying quartet states of Ga•N_2, it was found that some of these states are charge-transfer states, Ga^+•N_2^-, with an activated NN bond (i.e., long NN bond). Preliminary results of some computed intermolecular GaN bond lengths and intermolecular vibrational frequencies suggest that some of these quartet states are reasonably strongly bound. Further investigation on the low-lying quartet states of the Ga•N_2 complex, which would contribute to the understanding of activation of dinitrogen by the metal atom, is underway.

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References and Notes

(1) Greetham, G. M.; Hanton, M. J.; Ellis, A. M. *PCCP* **1999**, *1*, 2703.

(2) Zhou, M.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 1648.

(3) Chaban, G.; Gordon, M. S. *J. Chem. Phys.* **1997**, *107*, 2160.

(4) Lee, E. P. F.; Dyke, J. M. Mok, D, K.W.; Chau, F.-T. In preparation.

(5) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Cliffoird, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombem, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*; Gaussian, Inc.: Pittsburgh, PA.

(7) Knowles, P. J.; Hampel, C.; Werner, H. J. *J. Chem. Phys*. **1993**, *99*, 5219.

(8) MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P. J.; with contributions from Almlöf, J.; Amos, R. D.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Elbert, S. T.; Hampel, C.; Lindh, R.; Lloyd, A. W.; Meyer, W.; Nicklass, A.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.; Mura, M. E.; Pulay, P.; Schütz, M.; Stoll, H.; Thorsteinsson, T.

(9) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(10) Wilson, A. K.; Woon. D. E.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys*. **1999**, *110*, 7667; basis sets were also obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA, and funded by the, U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institue for the, U.S. Department of Energy under contract DE-AC06−76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

(11) Partridge, H. *J. Chem. Phys*. **1989**, *90*, 1043.

(12) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards Circular 467; U.S. Department of Commerce: Washington, DC, 1949.

(13) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1984; p 1.