

## FEATURE ARTICLE

## Periodicity and Peculiarity in 120 First- and Second-Row Diatomic Molecules

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Received: April 12, 1994; In Final Form: June 20, 1994<sup>®</sup>

The ground and very low-lying excited states of all 120 first- and second-row diatomic molecules are surveyed. Three quarters of these molecules have had their ground state term symbols reliably experimentally determined. However, one quarter remain predicted only theoretically. For all 120 species, the best available experimental (where known) and theoretical values for the dissociation energies to ground state atoms are also presented. The Aufbau principle, combined with standard energy ordering for the valence molecular orbitals, is able to properly account for the ground state term symbols of all but 20 of the diatomics studies. The 20 exceptions produce higher than expected ground state spin multiplicity and arise when there are 4–5 or 7–8 valence electrons and group 3, 4, or 5 (but not group 6 or 7) atoms are involved.

## I. Introduction

One might expect that essentially all of the  $15 \times 16/2 = 120$  diatomic molecules comprised of first (H, Li, ..., F) and second (Na, ..., Cl) row atoms have been thoroughly studied to the extent that their ground electronic states and the corresponding bond lengths ( $R_e$ ) and dissociation energies ( $D_e$ ) are well established. However, such is not the case; in Figure 1 those diatomics for which even the ground electronic states have not been so characterized are displayed in burgundy. In purple are shown the diatomics whose ground electronic states are reasonably well characterized. Most of the experimental data used to create Figure 1 were taken from the monograph of Huber and Herzberg,<sup>1</sup> although several species' properties were obtained from more recent sources.<sup>2–9</sup> It probably surprises most students of chemistry to learn that more than one quarter of all the diatomic molecules formed by combining pairs of first- or second-row atoms have yet to be experimentally characterized. Many of the uncharacterized diatomic molecules are very reactive intermediates with unpaired electrons or unsaturated valences of one or both atoms, which therefore can exist and be studied only under special conditions.

In this article, we consider the electronic structures of the ground and low-lying excited states of diatomic molecules composed of atoms from the first and second rows, including

the corresponding hydrides but excluding rare-gas-containing species. We emphasize (i) species that have yet to be studied experimentally, (ii) species whose ground states do not involve maximal double orbital occupancy, (iii) trends and exceptions to trends in the spin multiplicity of ground states.

Sophisticated *ab initio* techniques were applied to many of the 33 experimentally uncharacterized diatoms shown in Figure 1 in burgundy. In particular, the following 23 have been studied in earlier theoretical works: LiB,<sup>10</sup> LiC,<sup>10c,11</sup> LiN,<sup>10c,12</sup> LiMg,<sup>13</sup> LiAl,<sup>10c</sup> LiSi,<sup>10c,11</sup> LiP,<sup>14</sup> LiS,<sup>15</sup> BeN,<sup>16</sup> BeC,<sup>17</sup> BeNa,<sup>13</sup> BeAl,<sup>13</sup> BeSi,<sup>11b</sup> BeP,<sup>14</sup> BP,<sup>14</sup> NaMg,<sup>13</sup> NaSi,<sup>10c</sup> NaP,<sup>14</sup> NaS,<sup>15</sup> MgSi,<sup>10c</sup> MgP,<sup>14</sup> AlP,<sup>14</sup> and SiP.<sup>14</sup> In the present work, we present our new results on the remaining 10 diatomic molecules: BeB, NaB, NaC, NaN, MgB, MgC, MgN, AlB, NaAl and MgAl. We repeat high-level calculations on several of the other 23 molecules for which the ground state has not yet been identified with certainty. In addition, we attempt to examine patterns in ground state spin multiplicity for the species in Figure 1, in particular noting circumstances where ground states with higher than expected spin multiplicities occur.

## II. Computational Details

The bond lengths and harmonic vibrational frequencies of the 10 diatomics (BeB, NaB, NaC, NaN, MgB, MgC, MgN, AlB, NaAl, and MgAl) for which new data are presented here were optimized using analytical gradients<sup>18</sup> and polarized split-

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1994.

	H	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl
H	H <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>														
Li	LiH 1Σ <sup>+</sup>	Li <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>													
Be	BeH 2Σ <sup>+</sup>	BeLi 2Σ <sup>+</sup>	Be <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>												
B	BH 1Σ <sup>+</sup>	BLi	BBe	B <sub>2</sub> 3Σ <sub>g</sub> <sup>-</sup>											
C	CH 2Π <sub>r</sub>	CLi	CBe	CB 4Σ <sup>-</sup>	C <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>										
N	NH 3Σ <sup>-</sup>	NLi	NBe	NB 3Π <sub>i</sub>	NC 2Σ <sup>+</sup>	N <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>									
O	OH 2Π <sub>i</sub>	OLi	OBe	OB 2Σ <sup>+</sup>	OC 1Σ <sup>+</sup>	ON 2Π <sub>r</sub>	O <sub>2</sub> 3Σ <sub>g</sub> <sup>-</sup>								
F	FH 1Σ <sup>+</sup>	FLi	FBe	FB 1Σ <sup>+</sup>	FC 2Π <sub>r</sub>	FN 3Σ <sup>-</sup>	FO 2Π <sub>i</sub>	F <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>							
Na	NaH 1Σ <sup>+</sup>	NaLi 1Σ <sup>+</sup>	NaBe	NaB	NaC	NaN	NaO 2Π <sub>i</sub>	NaF 1Σ <sup>+</sup>	Na <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>						
Mg	MgH 2Σ <sup>+</sup>	MgLi	MgBe 1Σ <sup>+</sup>	MgB	MgC	MgN	MgO 1Σ <sup>+</sup>	MgF 2Σ <sup>+</sup>	MgNa	Mg <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>					
Al	AlH 1Σ <sup>+</sup>	AlLi	AlBe	AlB	AlC 4Σ <sup>-</sup>	AlN 3Π <sub>i</sub>	AlO 2Σ <sup>+</sup>	AlF 1Σ <sup>+</sup>	AlNa	AlMg	Al <sub>2</sub> 3Π <sub>u</sub>				
Si	SiH 2Π <sub>r</sub>	SiLi	SiBe	SiB 4Σ <sup>-</sup>	SiC 3Π <sub>i</sub>	SiN 2Σ <sup>+</sup>	SiO 1Σ <sup>+</sup>	SiF 2Π <sub>r</sub>	SiNa	SiMg	SiAl 4Σ <sup>-</sup>	Si <sub>2</sub> 3Σ <sub>g</sub> <sup>-</sup>			
P	PH 3Σ <sup>-</sup>	PLi	PBe	PB	PC 2Σ <sup>+</sup>	PN 1Σ <sup>+</sup>	PO 2Π <sub>r</sub>	PF 3Σ <sup>-</sup>	PNa	PMg	PAI	PSi	P <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>		
S	SH 2Π <sub>i</sub>	SLi	SBe 1Σ <sup>+</sup>	SB 2Σ <sup>+</sup>	SC 1Σ <sup>+</sup>	SN 2Π <sub>r</sub>	SO 3Σ <sup>-</sup>	SF 2Π <sub>i</sub>	SNa	SMg 1Σ <sup>+</sup>	SAI 2Σ <sup>+</sup>	SSi 1Σ <sup>+</sup>	SP 2Π <sub>r</sub>	S <sub>2</sub> 3Σ <sub>g</sub> <sup>-</sup>	
Cl	ClH 1Σ <sup>+</sup>	CLi 1Σ <sup>+</sup>	CBe 2Σ <sup>+</sup>	CIB 1Σ <sup>+</sup>	CIC 2Π <sub>r</sub>	CIN 3Σ <sup>-</sup>	CIO 2Π <sub>i</sub>	ClF 1Σ <sup>+</sup>	ClNa 1Σ <sup>+</sup>	ClMg 2Σ <sup>+</sup>	ClAl 1Σ <sup>+</sup>	ClSi 2Π <sub>r</sub>	CIP 3Σ <sup>-</sup>	CIS 2Π <sub>i</sub>	Cl <sub>2</sub> 1Σ <sub>g</sub> <sup>+</sup>

**Figure 1.** Experimentally determined ground electronic states of diatomic molecules composed of first- and second-row atoms (including hydrides). The diatomic molecules with experimentally unknown ground electronic states marked in burgundy.

valence basis sets of 6-311+G\*<sup>19</sup> quality at the correlated MP2-(full) level (UMP2(full) for open-shell systems) of theory. The resulting MP2 (full)/6-311+G\* equilibrium geometries were then used to further evaluate electron correlation corrections, in the frozen-core approximation, by Møller–Plesset perturbation theory to full fourth order<sup>20</sup> and by the (U)QCISD(T) method<sup>21</sup> using the 6-311+G(2df) basis sets for Li to F and Na to Cl. The UHF wave functions for open-shell systems were spin-projected to produce pure spectroscopic states (PUHF, PMP2, PMP3, and PMP4).<sup>22</sup> The geometries of selected low-lying excited electronic states were optimized then at the QCISD(T)/6-311+G(2df) level. All calculations were carried out with the GAUSSIAN 92<sup>23</sup> suite of programs unless otherwise specified, and core orbitals were kept frozen in all correlated calculations.

The geometries and harmonic vibrational frequencies of several diatomics that have two electronic states within 5 kcal/mol of one another were also studied using the complete active self-consistent field–multireference configuration interaction method, including all single and double excitations from the

reference configurations (CASSCF–MRCISD).<sup>24,25</sup> In diatomic molecules treated by CASSCF and CASSCF–MRCISD calculations in C<sub>2v</sub> symmetry, the first (a<sub>1</sub>) representation contains both σ and δ orbitals, the second (b<sub>1</sub>) and third (b<sub>2</sub>) contain π<sub>x</sub> and π<sub>y</sub> orbitals, respectively, and the fourth (a<sub>2</sub>) contains δ orbitals. Because we used different active spaces for different molecules, we present the details of each calculation when discussed specifically later. For the CASSCF–MRCISD calculations, we used the very large ANO basis set of Widmark et al.<sup>26</sup> These calculations were performed using the MOLCAS-2 program.<sup>27</sup>

The MgAl and BAl molecules were also studied at the MCSCF level using Dunning's augmented correlation consistent polarized valence basis sets (aug-cc-pVDZ)<sup>28</sup> and the GAMESS<sup>29</sup> program. Details of the configuration spaces employed will be given in the description of the properties of these molecules.

The ground and low-lying state results for the 10 newly examined diatoms as well as for five others examined by earlier workers and reexamined here are summarized in Tables 1–15.

TABLE 1: Calculated Molecular Properties of the Lowest BeB States

BeB( $^2\Pi_r$ )	BeB( $^2\Sigma^+$ )	BeB( $^4\Pi_r$ )	BeB( $^4\Sigma^-$ )	BeB( $^2\Pi_i$ )
$1\sigma^2 2\sigma^1 1\pi^1$	$1\sigma^2 2\sigma^2 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^2$	$1\sigma^2 1\pi^3$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -39.22194$	$E_{MP2} = -39.21715$	$E_{MP2} = -39.22489$	$E_{MP2} = -39.21787$	$E_{MP2} = -39.112071$
$R_e(\text{Be-B}) = 1.922 \text{ \AA}$	$R_e(\text{Be-B}) = 2.085 \text{ \AA}$	$R_e(\text{Be-B}) = 1.828 \text{ \AA}$	$R_e(\text{Be-B}) = 1.684 \text{ \AA}$	$R_e(\text{Be-B}) = 1.492 \text{ \AA}$
$\omega_e = 680 \text{ cm}^{-1}$	$\omega_e = 575 \text{ cm}^{-1}$	$\omega_e = 839 \text{ cm}^{-1}$	$\omega_e = 1102 \text{ cm}^{-1}$	$\omega_e = 1392 \text{ cm}^{-1}$
$\langle S^2 \rangle = 0.759$	$\langle S^2 \rangle = 0.772$	$\langle S^2 \rangle = 3.755$	$\langle S^2 \rangle = 3.836$	$\langle S^2 \rangle = 0.944$
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*
$R_e(\text{Be-B}) = 1.962 \text{ \AA}$	$R_e(\text{Be-B}) = 2.113 \text{ \AA}$	$R_e(\text{Be-B}) = 1.833 \text{ \AA}$	$R_e(\text{Be-B}) = 1.719 \text{ \AA}$	$R_e(\text{Be-B}) = 1.492 \text{ \AA}$
$E_{PMP4} = -39.23609$	$E_{PMP4} = -39.22352$	$E_{PMP4} = -39.22073$	$E_{PMP4} = -39.21852$	$E_{PMP4} = -39.12571$
$E_{QCISD(T)} = -39.24471$	$E_{QCISD(T)} = -39.23011$	$E_{QCISD(T)} = -39.22407$	$E_{QCISD(T)} = -39.22319$	
$\langle S^2 \rangle = 0.763$	$\langle S^2 \rangle = 0.776$	$\langle S^2 \rangle = 3.757$	$\langle S^2 \rangle = 3.862$	$\langle S^2 \rangle = 0.938$
$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 7.9 \text{ kcal/mol}$	$T_{ePMP4} = 9.6 \text{ kcal/mol}$	$T_{ePMP4} = 11.0 \text{ kcal/mol}$	$T_{ePMP4} = 69.3 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 9.2 \text{ kcal/mol}$	$T_{eQCISD(T)} = 13.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 13.5 \text{ kcal/mol}$	

TABLE 2: Calculated Molecular Properties of the Lowest NaB States

NaB( $^3\Pi_r$ )	NaB( $^1\Sigma^+$ )	NaB( $^3\Sigma^-$ )
$1\sigma^2 1\pi^1 2\sigma^1$	$1\sigma^2 2\sigma^2$	$1\sigma^2 1\pi^2$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -186.58768$	$E_{MP2} = -186.57336$	$E_{MP2} = -186.56706$
$R_e(\text{Na-B}) = 2.490 \text{ \AA}$	$R_e(\text{Na-B}) = 2.708 \text{ \AA}$	$R_e(\text{Na-B}) = 2.287 \text{ \AA}$
$\omega_e = 354 \text{ cm}^{-1}$	$\omega_e = 302 \text{ cm}^{-1}$	$\omega_e = 407 \text{ cm}^{-1}$
$\langle S^2 \rangle = 2.013$		$\langle S^2 \rangle = 2.063$
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*
$R_e(\text{Na-B}) = 2.520 \text{ \AA}$	$R_e(\text{Na-B}) = 2.770 \text{ \AA}$	$R_e(\text{Na-B}) = 2.287 \text{ \AA}$
$E_{PMP4} = -186.46799$	$E_{PMP4} = -186.45970$	$E_{PMP4} = -186.44770$
$E_{QCISD(T)} = -186.47046$	$E_{QCISD(T)} = -186.46549$	$E_{QCISD(T)} = -186.45230$
$\langle S^2 \rangle = 2.016$		$\langle S^2 \rangle = 2.059$
$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 5.2 \text{ kcal/mol}$	$T_{ePMP4} = 12.7 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 3.1 \text{ kcal/mol}$	$T_{eQCISD(T)} = 11.4 \text{ kcal/mol}$
CASSCF-MRCISD	CASSCF-MRCISD	
$R_e(\text{Na-B}) = 2.526 \text{ \AA}$	$R_e(\text{Na-B}) = 2.757 \text{ \AA}$	
$\omega_e = 329 \text{ cm}^{-1}$	$\omega_e = 255 \text{ cm}^{-1}$	
$E_{\text{CASSCF-MRCISD}} = -186.48765$	$E_{\text{CASSCF-MRCISD}} = -186.48361$	
$T_{e\text{CASSCF-MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD}} = 2.5 \text{ kcal/mol}$	
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)	
$R_e(\text{Na-B}) = 2.526 \text{ \AA}$	$R_e(\text{Na-B}) = 2.755 \text{ \AA}$	
$\omega_e = 329 \text{ cm}^{-1}$	$\omega_e = 255 \text{ cm}^{-1}$	
$E_{\text{CASSCF-MRCISD(Q)}} = -186.48847$	$E_{\text{CASSCF-MRCISD(Q)}} = -186.48421$	
$T_{e\text{CASSCF-MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD(Q)}} = 2.7 \text{ kcal/mol}$	

### III. Results and Discussions

#### A. The 10 as Yet Uncharacterized Diatomics. BeB.

Assuming doubly occupancy for the  $1\sigma$  valence orbital, the three other valence electrons may be distributed throughout the lowest  $2\sigma$ ,  $3\sigma$ , and  $1\pi$  valence orbitals giving five possible occupancies:  $1\sigma^2 2\sigma^1 1\pi^1$ ,  $1\sigma^2 2\sigma^2 3\sigma^1$ ,  $1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$ ,  $1\sigma^2 2\sigma^1 1\pi^2$ , and  $1\sigma^2 1\pi^3$ , which lead to several low-lying electronic states:  $^2\Pi_r$  ( $1\sigma^2 2\sigma^1 1\pi^1$ ),  $^2\Sigma^+$  ( $1\sigma^2 2\sigma^2 3\sigma^1$ ),  $^2\Pi_r$  and  $^4\Pi_r$  ( $1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$ ),  $^4\Sigma^-$ ,  $^2\Sigma^-$  and  $^2\Delta$  ( $1\sigma^2 2\sigma^1 1\pi^2$ ), and  $^2\Pi_i$  ( $1\sigma^2 1\pi^3$ ). Preliminary calculations at the MP2(full)/6-311+G\* level were carried out for  $^2\Pi_r$ ,  $^2\Sigma^+$ ,  $^4\Pi_r$ ,  $^4\Sigma^-$ , and  $^2\Pi_i$  states with the  $^4\Pi_r$  state proving to be the lowest (Table 1). However, when larger basis sets and more sophisticated correlation methods (QCISD(T)/6-311+G(2df)) were used, the  $^2\Pi_r$  state was predicted to be the ground state and the  $^2\Sigma^+$  state to be the first excited state. The  $^4\Pi_r$  and  $^4\Sigma^-$  states are the next excited states. For BeB we are confident that the  $^2\Pi_r$  state is the ground electronic state because (i) all four low-lying states have small spin contaminations, (ii) the energy difference between the ground electronic state and the first excited state is 8–9 kcal/mol, and (iii) the relative energy difference between PMP4 and QCISD(T) is only 1.3 kcal/mol, less than the first excitation energy. The calculated dissociation energy ( $D_e$ ) of BeB( $^2\Pi_r$ ) is 1.57 eV at the QCISD(T)/6-311+G(2df) level.

**NaB.** Given a total of four valence electrons and assuming double occupancy for the  $1\sigma$  orbital, the only three low-energy

configurations involve  $1\sigma^2 2\sigma^2$ ,  $1\sigma^2 2\sigma^1 1\pi^1$ , and  $1\sigma^2 1\pi^2$  occupancies all of which have been studied. The results appear in Table 2 where we find the *high-spin*  $^3\Pi_r$  ( $1\sigma^2 2\sigma^1 1\pi^1$ ) state to be the ground state and the low-spin  $^1\Sigma^+$  ( $1\sigma^2 2\sigma^2$ ) state to be the lowest-lying excited state at both the PMP4 and QCISD(T) levels.

Because the adiabatic  $X^3\Pi_r \rightarrow ^1\Sigma^+$  excitation energy is rather small, 3.1 kcal/mol, we carried out calculations using the CASSCF-MRCISD(Q) method and the  $(17s12p5d4f/7s5p3d2f)_{\text{Na}} + (14s9p4d3f/7s5p3d2f)_{\text{B}}$  basis set. The CASSCF expansion included 152 ( $^1\Sigma^+$ ) and 160 ( $^3\Pi_r$ ) configurations, which represent all possible excitations of all four valence electrons among (4,2,2,1) active orbitals respectively of  $a_1$ ,  $b_1$ ,  $b_2$ , and  $a_2$  representations of  $C_{2v}$  symmetry. All single and double excitations from these 152 and 160 CASSCF configurations were then included in the MRCISD calculations giving the 86 114 ( $^1\Sigma^+$ ) and 117 475 ( $^3\Pi_r$ ) MRCISD configurations. Davidson's corrections to the MRCISD energies were very small, and as a result the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels are very close to each other (Table 2). Moreover, the  $^3\Pi_r$  state is the ground state and  $^1\Sigma^+$  is the first excited state at both the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels. The ground electronic state is well represented by the single Hartree-Fock electronic configuration ( $C_{\text{HF}}(1\sigma^2 2\sigma^1 1\pi^1) = 0.9525$ ), which is the only configuration in the MRCISD expansion that has a coefficient larger than 0.15.

**TABLE 3: Calculated Molecular Properties of the Lowest NaC States**

NaC( $^4\Sigma^-$ )	NaC( $^2\Pi_i$ )	NaC( $^2\Pi_i$ )
$1\sigma^21\pi^22\sigma^1$	$1\sigma^22\sigma^21\pi^1$	$1\sigma^21\pi^3$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -199.80955$	$E_{MP2} = -199.74712$	$E_{MP2} = -199.71752$
$R_e(\text{Na}-\text{C}) = 2.251 \text{ \AA}$	$R_e(\text{Na}-\text{C}) = 2.505 \text{ \AA}$	$R_e(\text{Na}-\text{C}) = 2.135 \text{ \AA}$
$\omega_e = 443 \text{ cm}^{-1}$	$\omega_e = 401 \text{ cm}^{-1}$	$\omega_e = 474 \text{ cm}^{-1}$
$\langle S^2 \rangle = 3.756$	$\langle S^2 \rangle = 0.815$	$\langle S^2 \rangle = 0.799$
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*
$R_e(\text{Na}-\text{C}) = 2.264 \text{ \AA}$	$R(\text{Na}-\text{C}) = 2.505 \text{ \AA}$	$R(\text{Na}-\text{C}) = 2.135 \text{ \AA}$
$E_{PMP4} = -199.69560$	$E_{MP4} = -199.64374$	$E_{MP4} = -199.61549$
$E_{QCISD(T)} = -199.69677$	$E_{QCISD(T)} = -199.64996$	$E_{QCISD(T)} = -199.62534$
$\langle S^2 \rangle = 3.756$	$\langle S^2 \rangle = 0.817$	$\langle S^2 \rangle = 0.792$
$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{eMP4} = 32.5 \text{ kcal/mol}$	$T_{eMP4} = 50.3 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 29.4 \text{ kcal/mol}$	$T_{eQCISD(T)} = 44.8 \text{ kcal/mol}$

**TABLE 4: Calculated Molecular Properties of the Lowest NaN States**

NaN( $^2\Sigma^-$ )	NaN( $^3\Pi_i$ )	NaN( $^1\Sigma^+$ )
$1\sigma^22\sigma^21\pi^2$	$1\sigma^21\pi^32\sigma^1$	$1\sigma^21\pi^4$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -216.47526$	$E_{MP2} = -216.47499$	$E_{MP2} = -216.39010$
$R_e(\text{Na}-\text{N}) = 2.591 \text{ \AA}$	$R_e(\text{Na}-\text{N}) = 2.104 \text{ \AA}$	$R_e(\text{Na}-\text{N}) = 2.011 \text{ \AA}$
$\omega_e = 144 \text{ cm}^{-1}$	$\omega_e = 484 \text{ cm}^{-1}$	$\omega_e = 475 \text{ cm}^{-1}$
$\langle S^2 \rangle = 2.895$	$\langle S^2 \rangle = 2.063$	
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*
$R_e(\text{Na}-\text{N}) = 2.287 \text{ \AA}$	$R_e(\text{Na}-\text{N}) = 2.120 \text{ \AA}$	$R(\text{Na}-\text{N}) = 2.011 \text{ \AA}$
$E_{PMP4} = -216.36767$	$E_{PMP4} = -216.37615$	$E_{MP4} = -216.29664$
$E_{QCISD(T)} = -216.38550$	$E_{QCISD(T)} = -216.37586$	$E_{QCISD(T)} = -216.30965$
$\langle S^2 \rangle = 2.837$	$\langle S^2 \rangle = 2.058$	
$T_{ePMP4} = 5.3 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{eMP4} = 44.6 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 6.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 47.6 \text{ kcal/mol}$
CASSCF-MRCISD	CASSCF-MRCISD	
$R_e(\text{Na}-\text{N}) = 2.282 \text{ \AA}$	$R_e(\text{Na}-\text{N}) = 2.117 \text{ \AA}$	
$\omega_e = 379 \text{ cm}^{-1}$	$\omega_e = 465 \text{ cm}^{-1}$	
$E_{\text{CASSCF-MRCISD}} = -216.41352$	$E_{\text{CASSCF-MRCISD}} = -216.40139$	
$T_{e\text{CASSCF-MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD}} = 7.6 \text{ kcal/mol}$	
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)	
$R_e(\text{Na}-\text{N}) = 2.284 \text{ \AA}$	$R_e(\text{Na}-\text{N}) = 2.121 \text{ \AA}$	
$\omega_e = 379 \text{ cm}^{-1}$	$\omega_e = 461 \text{ cm}^{-1}$	
$E_{\text{CASSCF-MRCISD(Q)}} = -216.41918$	$E_{\text{CASSCF-MRCISD(Q)}} = -216.40621$	
$T_{e\text{CASSCF-MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD(Q)}} = 8.1 \text{ kcal/mol}$	

The occupancies of the natural MOs for the  $^3\Pi_r$  state are  $1\sigma^{1.89}2\sigma^{0.98}3\sigma^{0.03}1\pi_x^{0.97}1\pi_y^{0.06}2\pi_x^{0.02}2\pi_y^{0.01}$ .

The  $^1\Sigma^+$  state is also well represented by the Hartree-Fock wave function ( $C_{\text{HF}}(1\sigma^22\sigma^1) = 0.9034$ ). However, in this case, one non-Hartree-Fock configuration has an expansion coefficient larger than 0.15:  $C(1\sigma^22\sigma^03\sigma^2) = 0.2707$ . The occupancies of the natural MOs for the  $^1\Sigma^+$  state are  $1\sigma^{1.88}2\sigma^{1.74}3\sigma^{0.07}1\pi_x^{0.07}1\pi_y^{0.07}2\pi_x^{0.01}2\pi_y^{0.01}$ .

We are confident that  $^3\Pi_r$  is the ground electronic state for NaB because we have very good agreement between the adiabatic  $^3\Pi_r \rightarrow ^1\Sigma^+$  excitation energies with all four sophisticated ab initio methods. The valence isoelectronic LiB molecule also has a  $X^3\Pi_r$  ground electronic state; however, other valence isoelectronic molecules such as LiAl and NaAl have singlet  $X^1\Sigma^+$  ground electronic states (see below). Finally, our calculated dissociation energy ( $D_e$ ) of NaB( $^3\Pi_r$ ) is 0.76 eV at the QCISD(T)/6-311+G(2df) level.

*NaC.* For this molecule, one might anticipate any of three valence orbital occupancies:  $1\sigma^22\sigma^21\pi^1$ ,  $1\sigma^22\sigma^1\pi^2$ , and  $1\sigma^21\pi^3$ . When the  $1\pi$  orbital is occupied by three electrons (essentially  $2p$  on C), we obtain a  $^2\Pi_i$  state. When two electrons occupy the  $1\pi$  orbital and the third electron occupies the antibonding  $2\sigma$  orbital (essentially  $2s2p$  hybrid orbital on C), a  $^4\Sigma^-$  state results. Finally, when two electrons occupy the  $2\sigma$  orbital and one electron occupies the  $1\pi$  orbital, a  $^2\Pi_r$  state results. Among all states with  $\pi^1$ ,  $\pi^2$ , and  $\pi^3$  occupancies, we found the *high-spin*  $^4\Sigma^-$  ( $1\sigma^21\pi^22\sigma^1$ ) state to be the lowest. The low-spin  $^2\Pi_r$

( $1\sigma^22\sigma^21\pi^1$ ) and  $^2\Pi_i$  ( $1\sigma^21\pi^3$ ) states are less stable by 29.4 and 44.8 kcal/mol, respectively (see Table 3). We feel confident in predicting that  $^4\Sigma^-$  is the ground electronic state of NaC. Because (i) the results for relative energies of these three electronic states agree well each other at the QCISD(T) and PMP4 levels, (ii) the spin contaminations in all three states are low, and (iii) the energy of the lowest excited  $^2\Pi_r$  electronic state is more than 1 eV. (The accuracy of relative energies obtained in our calculations at the QCISD(T)/6-311+G(2df) level is ca. 0.3 eV.) The valence isoelectronic LiC, LiSi, and NaSi diatomics also have ( $^4\Sigma^-$ ) ground electronic states. Our calculated dissociation energy ( $D_e$ ) of NaC( $^4\Sigma^-$ ) is 1.97 eV at the QCISD(T)/6-311+G(2df) level.

*NaN.* For this molecule, three low-lying states have been studied:  $^3\Sigma^-$  ( $1\sigma^22\sigma^21\pi^2$ ),  $^3\Pi_i$  ( $1\sigma^22\sigma^11\pi^3$ ), and  $^1\Sigma^+$  ( $1\sigma^21\pi^4$ ) (Table 4). At the PMP4 and QCISD(T) levels, the  $^1\Sigma^+$  is well separated from the others in energy. Because the  $^3\Pi_i$  state is lower in energy than the  $^3\Sigma^-$  state at the PMP4 level while the  $^3\Sigma^-$  state is lower than the  $^3\Pi_i$  state at the QCISD(T) level, we carried out large scale CASSCF-MRCISD(T) calculations using  $(17s12p5d4f/7s5p3d2f)_{\text{Na}} + (14s9p4d3f/7s5p3d2f)_{\text{N}}$  basis sets for these two states. The CASSCF expansions included 378 ( $^3\Sigma^-$ ) and 384 ( $^3\Pi_i$ ) configurations, which represent all possible occupations of six valence electrons in (4,2,2,1) active orbitals. All single and double excitations from these 378 and 384 CASSCF configurations were then included in the MRCISD calculations giving 1 115 606 ( $^3\Sigma^-$ ) and 1 154 220 ( $^3\Pi_i$ ) MR-

TABLE 5: Calculated Molecular Properties of the Lowest MgB States

MgB( $^2\Pi_r$ )	MgB( $^2\Sigma^+$ )	MgB( $^4\Pi_r$ )	MgB( $^4\Sigma^-$ )	MgB( $^2\Pi_i$ )
$1\sigma^2 2\sigma^2 1\pi^1$	$1\sigma^2 2\sigma^2 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$	$1\sigma^2 1\pi^2 2\sigma^1$	$1\sigma^2 1\pi^3$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -224.351227$		$E_{MP2} = -224.33561$	$E_{MP2} = -224.32603$	$E_{MP2} = -224.20474$
$R_e(\text{Mg}-\text{B}) = 2.473 \text{ \AA}$	no minimum	$R_e(\text{Mg}-\text{B}) = 2.263 \text{ \AA}$	$R_e(\text{Mg}-\text{B}) = 2.117 \text{ \AA}$	$R_e(\text{Mg}-\text{B}) = 1.983 \text{ \AA}$
$\omega_e = 269 \text{ cm}^{-1}$		$\omega_e = 510 \text{ cm}^{-1}$	$\omega_e = 568 \text{ cm}^{-1}$	$\omega_e = 630 \text{ cm}^{-1}$
$\langle S^2 \rangle = 0.768$		$\langle S^2 \rangle = 3.757$	$\langle S^2 \rangle = 3.881$	$\langle S^2 \rangle = 3.881$
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*
$R_e(\text{Mg}-\text{B}) = 2.390 \text{ \AA}$	$R_e(\text{Mg}-\text{B}) = 2.775 \text{ \AA}$	$R_e(\text{Mg}-\text{B}) = 2.263 \text{ \AA}$	$R_e(\text{Mg}-\text{B}) = 2.117 \text{ \AA}$	$R_e(\text{Mg}-\text{B}) = 1.983 \text{ \AA}$
$E_{MP4} = -224.24634$	$E_{MP4} = -224.23560$	$E_{PMP4} = -224.21964$	$E_{PMP4} = -224.21417$	$E_{MP4} = -224.10592$
$E_{QCISD(T)} = -224.25419$	$E_{QCISD(T)} = -224.23962$	$E_{QCISD(T)} = -224.22283$	$E_{QCISD(T)} = -224.22221$	
$\langle S^2 \rangle = 0.768$	$\langle S^2 \rangle = 0.859$	$\langle S^2 \rangle = 3.759$	$\langle S^2 \rangle = 3.821$	$\langle S^2 \rangle = 1.672$
$T_{eMP4} = 0.0 \text{ kcal/mol}$	$T_{eMP4} = 6.7 \text{ kcal/mol}$	$T_{ePMP4} = 16.8 \text{ kcal/mol}$	$T_{ePMP4} = 20.2 \text{ kcal/mol}$	$T_{eMP4} = 88.1 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 9.1 \text{ kcal/mol}$	$T_{eQCISD(T)} = 19.7 \text{ kcal/mol}$	$T_{eQCISD(T)} = 20.1 \text{ kcal/mol}$	

CISD configurations. Davidson's corrections to the MRCISD energies were very small, and thus our results at the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels are very close to each other (Table 4).

The  $^3\Sigma^-$  state was predicted to be the ground state at both levels with an excitation energy  $^3\Sigma^- \rightarrow ^3\Pi_i$  of ca. 8 kcal/mol (see Table 4). Both the  $^3\Pi_i$  and the  $^3\Sigma^-$  states are well represented by Hartree-Fock wave functions ( $C_{HF}(1\sigma^2 2\sigma^2 - 1\pi_x^{\alpha} 1\pi_y^{\alpha}) = 0.9568$  for  $^3\Pi_i$  and  $C_{HF}(1\sigma^2 2\sigma^2 1\pi_x^{\alpha} 1\pi_y^{\alpha}) = 0.9452$  for  $^3\Sigma^-$ ). From more than 1 000 000 configurations, only the Hartree-Fock configurations have coefficients larger than 0.15. The occupancies of the natural MO for the  $^3\Pi_i$  and  $^3\Sigma^-$  states are  $1\sigma^{2.00} 2\sigma^{1.96} 3\sigma^{0.99} 4\sigma^{0.02} 1\pi_x^{0.99} 1\pi_y^{1.92} 2\pi_x^{0.01} 2\pi_y^{0.05}$  and  $1\sigma^{2.00} 2\sigma^{1.96} 3\sigma^{1.89} 4\sigma^{0.08} 1\pi_x^{0.99} 1\pi_y^{0.99} 2\pi_x^{0.01} 2\pi_y^{0.01}$ , respectively.

Because the  $^3\Sigma^-$  state has the lowest energy relative to the other states using all our sophisticated ab initio methods (QCISD(T), CASSCF-MRCISD, and CASSCF-MRCISD(Q)), we are confident that the  $^3\Sigma^-$  state is the ground electronic state of NaN. The valence isoelectronic LiN molecule also has a  $^3\Sigma^-$  ground state.<sup>10c</sup> Our calculated dissociation energy ( $D_e$ ) of NaN( $^3\Sigma^-$ ) is 0.77 eV at the QCISD(T)/6-311+G(2df) level.

**MgB.** This molecule is isoelectronic with BeB which we discussed earlier. On the basis of our BeB findings, we studied the following electronic states:  $^2\Pi_r$  ( $1\sigma^2 2\sigma^2 1\pi^1$ ),  $^2\Sigma^+$  ( $1\sigma^2 2\sigma^2 3\sigma^1$ ),  $^4\Pi_r$  ( $1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$ ),  $^4\Sigma^-$  ( $1\sigma^2 2\sigma^1 1\pi^2$ ), and  $^2\Pi_i$  ( $1\sigma^2 1\pi^3$ ). Preliminary calculations on these states at the MP2(full)/6-311+G\* level predict the  $^2\Pi_r$  state to be the lowest (Table 5). The  $^2\Pi_r$  state was also found to be the ground state when larger basis sets and more sophisticated correlation methods (PMP4 and QCISD(T) with 6-311+G(2df) basis sets) were used. The  $^2\Sigma^+$  state is predicted to be the first excited state, with the  $^4\Pi_r$  and  $^4\Sigma^-$  states lying higher in energy.

For MgB we are confident that the  $^2\Pi_r$  state is the ground electronic state because (i) all four low-lying states have small spin contamination, (ii) the energy difference between the ground state and the first excited state is 7–9 kcal/mol, and (iii) the relative energy difference between results at the PMP4 and QCISD(T) levels is only 2.4 kcal/mol, which is less than the first excitation energy. Our calculated dissociation energy ( $D_e$ ) of MgB( $^2\Pi_r$ ) is 0.47 eV at the QCISD(T)/6-311+G(2df) level.

**MgC.** Given a total of six valence electrons ( $3s^2$  from Mg and  $2s^2 2p^2$  from C), the most likely candidates for low-energy configurations involve  $1\sigma^2 2\sigma^2 1\pi^2$ ,  $1\sigma^2 2\sigma^1 1\pi^3$ ,  $1\sigma^2 1\pi^4$ , or  $1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$  occupancies. We therefore studied the following five low-lying electronic states for MgC:  $^3\Sigma^-$  ( $1\sigma^2 2\sigma^2 1\pi^2$ ),  $^3\Pi_i$  ( $1\sigma^2 2\sigma^1 1\pi^3$ ),  $^1\Sigma^+$  ( $1\sigma^2 1\pi^4$ ),  $^3\Pi_r$  ( $1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$ ), and  $^5\Sigma^-$  ( $1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$ ), and the results of our calculations appear in Table 6.

We find the  $^3\Sigma^-$  ( $1\sigma^2 2\sigma^2 1\pi^2$ ) state to be the ground state and the  $^5\Sigma^-$  ( $1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$ ) state to be the lowest-lying excited state at both the PMP4 and QCISD(T) levels. However, the adiabatic excitation  $^3\Sigma^- \rightarrow ^5\Sigma^-$  energy varies from 1.0 kcal/mol at the PMP4 level to 10.5 kcal/mol at the QCISD(T) level. Therefore, we also carried out calculations on these two states at the CASSCF-MRCISD(Q) level using a  $(17s12p5d4f/7s5p3d2f)_{Mg} + (14s9p4d3f/7s5p3d2f)_C$  basis set. The CASSCF expansion included 260 ( $^5\Sigma^-$ ) and 378 ( $^3\Sigma^-$ ) configurations, which represent all possible distributions of the six valence electrons, among the (4,2,2,1) and (3,2,2,1) active orbitals, respectively. All single and double excitations from these 260 and 378 CASSCF configurations were then included in the MRCISD calculations, giving the 852 680 ( $^5\Sigma^-$ ) and 1 155 606 ( $^3\Sigma^-$ ) MRCISD configurations. Davidson's corrections to the MRCISD energy were modest so results at the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels are reasonably close (Table 6). Because the  $^3\Sigma^-$  state has the lowest energy at all four of our most sophisticated ab initio levels, we are confident that  $^3\Sigma^-$  is the ground electronic state for MgC. Our calculated dissociation energy ( $D_e$ ) for MgC( $^3\Sigma^-$ ) is 1.50 eV at the QCISD(T)/6-311+G(2df) level.

After our calculations were completed, an article by Bauschlicher, Langhoff, and Partridge (BLP)<sup>30</sup> appeared in the literature reporting high-quality calculations on low-lying electronic states of MgC. These workers also found  $^3\Sigma^-$  to be the ground state and  $^5\Sigma^-$  to be the first excited state. Our results for the ground electronic state  $^3\Sigma^-$  ( $R_e(\text{Mg}-\text{C}) = 2.099 \text{ \AA}$ ,  $D_e = 1.50 \text{ eV}$ , and  $\Delta G_{1/2} = 527 \text{ cm}^{-1}$ ) agree well with the BLP data ( $R_e(\text{Mg}-\text{C}) = 2.103 \text{ \AA}$ ,  $D_e = 1.52 \text{ eV}$ , and  $\Delta G_{1/2} = 541 \text{ cm}^{-1}$ ); however, for the first excited state, our data  $^5\Sigma^-$  ( $R_e(\text{Mg}-\text{C}) = 2.066 \text{ \AA}$ ,  $D_e = 1.01 \text{ eV}$ ,  $T_e = 3975 \text{ cm}^{-1}$ , and  $\Delta G_{1/2} = 570 \text{ cm}^{-1}$ ) are somewhat different from those of BLP ( $R_e(\text{Mg}-\text{C}) = 2.109 \text{ \AA}$ ,  $D_e = 0.66 \text{ eV}$ ,  $T_e = 3545 \text{ cm}^{-1}$ , and  $\Delta G_{1/2} = 515 \text{ cm}^{-1}$ ). The quite substantial difference in the bond length (0.043  $\text{\AA}$ ) and  $\Delta G_{1/2}$  (55  $\text{cm}^{-1}$ ) values is strange because, for the  $^5\Sigma^-$  state, we have good agreement for these quantities using four MP2(full), QCISD(T), CASSCF-MRCISD, and CASSCF-MRCISD(Q) different methods.

**MgN.** Given a total of seven valence electrons ( $3s^2$  from Mg and  $2s^2 2p^3$  from N), the most likely candidates for low-energy configurations involve  $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$ ,  $1\sigma^2 2\sigma^2 1\pi^3$ ,  $1\sigma^2 2\sigma^1 1\pi^3 3\sigma^1$ , and  $1\sigma^2 2\sigma^1 1\pi^4$  occupancies. We therefore studied the following four low-lying electronic states:  $^4\Sigma^-$  ( $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$ ),  $^2\Pi_i$  ( $1\sigma^2 2\sigma^2 1\pi^3$ ),  $^4\Pi_i$  ( $1\sigma^2 2\sigma^1 1\pi^3 3\sigma^1$ ), and  $^2\Sigma^+$  ( $1\sigma^2 2\sigma^1 1\pi^4$ ). The results of our calculations appear in Table 7.

We found the *high-spin*  $^4\Sigma^-$  ( $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$ ) state to be the ground electronic state and the  $^2\Pi_i$  ( $1\sigma^2 2\sigma^2 1\pi^3$ ) state to be the lowest-lying excited state. However, the adiabatic  $X^4\Sigma^- \rightarrow ^2\Pi_i$

**TABLE 6: Calculated Molecular Properties of the Lowest MgC States**

MgC( $^3\Sigma^-$ )	MgC( $^5\Sigma^-$ )	MgC( $^3\Pi_r$ )	MgC( $^3\Pi_i$ )	MgC( $^1\Sigma^+$ )
$1\sigma^22\sigma^21\pi^2$	$1\sigma^22\sigma^11\pi^23\sigma^1$	$1\sigma^22\sigma^21\pi^13\sigma^1$	$1\sigma^21\pi^32\sigma^1$	$1\sigma^21\pi^4$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -237.54866$	$E_{MP2} = -237.56361$	$E_{MP2} = -237.51941$	$E_{MP2} = -237.47165$	$E_{MP2} = -237.39050$
$R_e(\text{Mg}-\text{C}) = 2.087 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 2.064 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 2.280 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 1.966 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 1.834 \text{ \AA}$
$\omega_e = 507 \text{ cm}^{-1}$	$\omega_e = 593 \text{ cm}^{-1}$	$\omega_e = 370 \text{ cm}^{-1}$	$\omega_e = 613 \text{ cm}^{-1}$	$\omega_e = 773 \text{ cm}^{-1}$
$\langle S^2 \rangle = 2.038$	$\langle S^2 \rangle = 6.006$	$\langle S^2 \rangle = 2.088$	$\langle S^2 \rangle = 2.041$	
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*
$R_e(\text{Mg}-\text{C}) = 2.083 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 2.062 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 2.280 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 1.966 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 1.834 \text{ \AA}$
$E_{PMP4} = -237.45647$	$E_{PMP4} = -237.45479$	$E_{PMP4} = -237.42256$	$E_{PMP4} = -237.37813$	$E_{PMP4} = -237.30181$
$E_{QCISD(T)} = -237.47358$	$E_{QCISD(T)} = -237.45680$	$E_{QCISD(T)} = -237.42660$	$E_{QCISD(T)} = -237.39372$	
$\langle S^2 \rangle = 2.035$	$\langle S^2 \rangle = 6.005$	$\langle S^2 \rangle = 2.087$	$\langle S^2 \rangle = 2.042$	
$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 1.0 \text{ kcal/mol}$	$T_{ePMP4} = 21.3 \text{ kcal/mol}$	$T_{ePMP4} = 48.1 \text{ kcal/mol}$	$T_{ePMP4} = 97.0 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 10.5 \text{ kcal/mol}$	$T_{eQCISD(T)} = 29.5 \text{ kcal/mol}$	$T_{eQCISD(T)} = 50.1 \text{ kcal/mol}$	
CASSCF-MRCISD	CASSCF-MRCISD			
$R_e(\text{Mg}-\text{C}) = 2.094 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 2.065 \text{ \AA}$			
$\omega_e = 543 \text{ cm}^{-1}$	$\omega_e = 573 \text{ cm}^{-1}$			
$E_{\text{CASSCF-MRCISD}} = -237.48796$	$E_{\text{CASSCF-MRCISD}} = -237.47211$			
$T_{e\text{CASSCF-MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD}} = 9.9 \text{ kcal/mol}$			
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)			
$R_e(\text{Mg}-\text{C}) = 2.099 \text{ \AA}$	$R_e(\text{Mg}-\text{C}) = 2.066 \text{ \AA}$			
$\omega_e = 536 \text{ cm}^{-1}$	$\omega_e = 572 \text{ cm}^{-1}$			
$E_{\text{CASSCF-MRCISD(Q)}} = -237.49350$	$E_{\text{CASSCF-MRCISD(Q)}} = -237.47539$			
$T_{e\text{CASSCF-MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD(Q)}} = 11.4 \text{ kcal/mol}$			

**TABLE 7: Calculated Molecular Properties of the Lowest MgN States**

MgN( $^4\Sigma^-$ )	MgN( $^2\Pi_i$ )	MgN( $^4\Pi_i$ )	MgN( $^2\Sigma^+$ )
$1\sigma^22\sigma^21\pi^23\sigma^1$	$1\sigma^22\sigma^21\pi^3$	$1\sigma^22\sigma^11\pi^33\sigma^1$	$1\sigma^22\sigma^11\pi^4$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -254.26138$	$E_{MP2} = -254.23191$	$E_{MP2} = -254.22690$	$E_{MP2} = -254.14261$
$R_e(\text{Mg}-\text{N}) = 2.068 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.857 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.944 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.847 \text{ \AA}$
$\omega_e = 574 \text{ cm}^{-1}$	$\omega_e = 827 \text{ cm}^{-1}$	$\omega_e = 619 \text{ cm}^{-1}$	$\omega_e = 637 \text{ cm}^{-1}$
$\langle S^2 \rangle = 3.806$	$\langle S^2 \rangle = 0.766$	$\langle S^2 \rangle = 3.766$	$\langle S^2 \rangle = 0.757$
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*	//MP2(full)/6-311+G*
$R_e(\text{Mg}-\text{N}) = 2.084 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.929 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.944 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.847 \text{ \AA}$
$E_{PMP4} = -254.16784$	$E_{PMP4} = -254.150029$	$E_{PMP4} = -254.13459$	$E_{PMP4} = -254.06134$
$E_{QCISD(T)} = -254.16932$	$E_{QCISD(T)} = -254.15924$	$E_{QCISD(T)} = -254.13590$	$E_{QCISD(T)} = -254.08554$
$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 11.2 \text{ kcal/mol}$	$T_{ePMP4} = 20.9 \text{ kcal/mol}$	$T_{ePMP4} = 66.8 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 6.3 \text{ kcal/mol}$	$T_{eQCISD(T)} = 21.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 52.6 \text{ kcal/mol}$
CASSCF-MRCISD	CASSCF-MRCISD		
$R_e(\text{Mg}-\text{N}) = 2.038 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.925 \text{ \AA}$		
$\omega_e = 942 \text{ cm}^{-1}$	$\omega_e = 631 \text{ cm}^{-1}$		
$E_{\text{CASSCF-MRCISD}} = -254.18311$	$E_{\text{CASSCF-MRCISD}} = -254.17687$		
$T_{e\text{CASSCF-MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD}} = 3.9 \text{ kcal/mol}$		
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)		
$R_e(\text{Mg}-\text{N}) = 2.133 \text{ \AA}$	$R_e(\text{Mg}-\text{N}) = 1.929 \text{ \AA}$		
$\omega_e = 730 \text{ cm}^{-1}$	$\omega_e = 627 \text{ cm}^{-1}$		
$E_{\text{CASSCF-MRCISD(Q)}} = -254.19718$	$E_{\text{CASSCF-MRCISD(Q)}} = -254.18630$		
$T_{e\text{CASSCF-MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF-MRCISD(Q)}} = 6.8 \text{ kcal/mol}$		

excitation energy is not large and varies from 11.2 kcal/mol at the PMP4 level to 6.3 kcal/mol at the QCISD(T) level. Therefore, we calculated the two states at the CASSCF-MRCISD(Q) level using a  $(17s12p5d4f/7s5p3d2f)_{\text{Mg}} + (14s-9p4d3f/7s5p3d2f)_{\text{N}}$  basis set. The CASSCF expansion included 104 ( $^4\Sigma^-$ ) and 196 ( $^2\Pi_i$ ) configurations, which represent all possible distributions of the seven valence electrons among the (3,2,2,0) active orbitals. All single and double excitations from the 104 ( $^4\Sigma^-$ ) and 196 ( $^2\Pi_i$ ) CASSCF configurations were then included in our MRCISD calculations giving 955 575 ( $^4\Sigma^-$ ) and 1 204 664 ( $^2\Pi_i$ ) MRCISD configurations.

The results are presented in Table 7. The  $^4\Sigma^-$  state has a lower energy than the  $^2\Pi_i$  state at both the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels. The  $^4\Sigma^-$  and  $^2\Pi_i$  states are not well represented by the Hartree-Fock wave function:  $C_{\text{HF}}(1\sigma^22\sigma^23\sigma^11\pi_x^\alpha1\pi_y^\alpha) = 0.3137$  and  $C(1\sigma^22\sigma^13\sigma^21\pi_x^\alpha1\pi_y^\alpha) = 0.8770$  for  $^4\Sigma^-$  and  $C_{\text{HF}}(1\sigma^22\sigma^21\pi_x^\alpha1\pi_y^2) = 0.8327$  for  $^2\Pi_i$  in

the MRCISD wave function at the optimal bond lengths. At  $R(\text{Mg}-\text{N}) = 2.100 \text{ \AA}$  and shorter distances, the dominant configuration in the  $^4\Sigma^-$  state is  $C_{\text{HF}}(1\sigma^22\sigma^23\sigma^11\pi_x^\alpha1\pi_y^\alpha) = 0.9526$ , and all other configurations in MRCISD expansion have coefficients less than 0.15 in magnitude. At the equilibrium internuclear distance, the  $1\sigma^22\sigma^23\sigma^11\pi_x^\alpha1\pi_y^\alpha$  configuration has a coefficient of 0.3137 while the  $C(1\sigma^22\sigma^13\sigma^21\pi_x^\alpha1\pi_y^\alpha) = 0.8770$  configuration is dominant with all others having amplitudes less than 0.15. The Davidson correction for this state is also different at short and long interatomic distances as a result of which the findings at the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels are quite different.

For the first excited  $^2\Pi_i$  state, the leading configuration ( $C_{\text{HF}}(1\sigma^22\sigma^23\sigma^01\pi_x^\alpha1\pi_y^2) = 0.8327$ ) remains the same along the potential energy curve, but two other configurations  $C(1\sigma^22\sigma^03\sigma^2-21\pi_x^\alpha1\pi_y^2) = -0.3482$  and  $C(1\sigma^22\sigma^03\sigma^01\pi_x^\beta1\pi_y^2) = -0.2806$  have amplitudes larger than 0.15. The occupancies of the

TABLE 8: Calculated Molecular Properties of the Lowest AIB States

AIB( $^3\Sigma^-$ )	AIB( $^3\Pi_r$ )	AIB( $^5\Sigma^-$ )
$1\sigma^2 2\sigma^2 1\pi^2$	$1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -266.67110$	$E_{MP2} = -266.67760$	$E_{MP2} = -266.65496$
$R_e(\text{Al-B}) = 2.019 \text{ \AA}$	$R_e(\text{Al-B}) = 2.212 \text{ \AA}$	$R_e(\text{Al-B}) = 1.943 \text{ \AA}$
$\omega_e = 651 \text{ cm}^{-1}$	$\omega_e = 521 \text{ cm}^{-1}$	$\omega_e = 792 \text{ cm}^{-1}$
$\langle S^2 \rangle = 2.644$	$\langle S^2 \rangle = 2.014$	$\langle S^2 \rangle = 6.002$
MCSCF/MCSCF	MCSCF/MCSCF	
$R_e(\text{Al-B}) = 2.088 \text{ \AA}$	$R_e(\text{Al-B}) = 2.261 \text{ \AA}$	
$\omega_e = 574 \text{ cm}^{-1}$	$\omega_e = 471 \text{ cm}^{-1}$	
$E_{MCSCF} = -266.50779$	$E_{MCSCF} = -266.50371$	
$T_{eMCSCF} = 0.0 \text{ kcal/mol}$	$T_{eMCSCF} = 2.6 \text{ kcal/mol}$	
QCISD(T)/6-311+g(2df)//	QCISD(T)/6-311+G(2df)//	QCISD(T)/6-311+G(2df)//
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	MP2(full)/6-311+G*
$R_e(\text{Al-B}) = 2.056 \text{ \AA}$	$R_e(\text{Al-B}) = 2.226 \text{ \AA}$	$R(\text{Al-B}) = 1.943 \text{ \AA}$
$E_{PMP4} = -266.57702$	$E_{PMP4} = -266.58174$	$E_{PMP4} = -266.54922$
$E_{QCISD(T)} = -266.58794$	$E_{QCISD(T)} = -266.58820$	$E_{QCISD(T)} = -266.55221$
$T_{ePMP4} = 3.0 \text{ kcal/mol}$	$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 17.4 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.2 \text{ kcal/mol}$	$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 22.6 \text{ kcal/mol}$
CASSCF-MRCISD	CASSCF-MRCISD	
$R_e(\text{Al-B}) = 2.046 \text{ \AA}$	$R_e(\text{Al-B}) = 2.224 \text{ \AA}$	
$\omega_e = 608 \text{ cm}^{-1}$	$\omega_e = 493 \text{ cm}^{-1}$	
$E_{CASSCF-MRCISD} = -266.60194$	$E_{CASSCF-MRCISD} = -266.59809$	
$T_{eCASSCF-MRCISD} = 0.0 \text{ kcal/mol}$	$T_{eCASSCF-MRCISD} = 2.4 \text{ kcal/mol}$	
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)	
$R_e(\text{Al-B}) = 2.051 \text{ \AA}$	$R_e(\text{Al-B}) = 2.237 \text{ \AA}$	
$\omega_e = 600 \text{ cm}^{-1}$	$\omega_e = 482 \text{ cm}^{-1}$	
$E_{CASSCF-MRCISD(Q)} = -266.60845$	$E_{CASSCF-MRCISD(Q)} = -266.60585$	
$T_{eCASSCF-MRCISD(Q)} = 0.0 \text{ kcal/mol}$	$T_{eCASSCF-MRCISD(Q)} = 1.6 \text{ kcal/mol}$	

TABLE 9: Calculated Molecular Properties of the Lowest NaAl States

NaAl( $^1\Sigma^+$ )	NaAl( $^3\Pi_r$ )	NaAl( $^3\Sigma^-$ )
$1\sigma^2 2\sigma^2$	$1\sigma^2 1\pi^1 2\sigma^1$	$1\sigma^2 1\pi^2$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -404.02294$	$E_{MP2} = -404.01938$	$E_{MP2} = -403.98789$
$R_e(\text{Na-Al}) = 3.134 \text{ \AA}$	$R_e(\text{Na-Al}) = 2.985 \text{ \AA}$	$R_e(\text{Na-Al}) = 2.673 \text{ \AA}$
$\omega_e = 196 \text{ cm}^{-1}$	$\omega_e = 184 \text{ cm}^{-1}$	$\omega_e = 259 \text{ cm}^{-1}$
	$\langle S^2 \rangle = 2.024$	$\langle S^2 \rangle = 2.044$
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)
$R_e(\text{Na-Al}) = 3.182 \text{ \AA}$	$R_e(\text{Na-Al}) = 3.007 \text{ \AA}$	$R_e(\text{Na-Al}) = 2.739 \text{ \AA}$
$E_{MP4} = -403.79651$	$E_{PMP4} = -403.79027$	$E_{PMP4} = -403.76274$
$E_{QCISD(T)} = -403.80002$	$E_{QCISD(T)} = -403.79176$	$E_{QCISD(T)} = -403.76424$
	$\langle S^2 \rangle = 2.027$	$\langle S^2 \rangle = 2.018$
$T_{eMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 3.9 \text{ kcal/mol}$	$T_{ePMP4} = 21.2 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 5.2 \text{ kcal/mol}$	$T_{eQCISD(T)} = 22.4 \text{ kcal/mol}$

natural MOs for the  $^4\Sigma^-$  and  $^2\Pi_i$  states are  $1\sigma^{1.96} 2\sigma^{1.91} 3\sigma^{0.99} 4\sigma^{0.03} 1\pi_x^{0.99} 1\pi_y^{0.99} 2\pi_x^{0.03} 2\pi_y^{0.03}$  and  $1\sigma^{1.96} 2\sigma^{1.60} 3\sigma^{0.38} 4\sigma^{0.02} 1\pi_x^{0.98} 1\pi_y^{1.91} 2\pi_x^{0.02} 2\pi_y^{0.07}$ , respectively. Because the  $^4\Sigma^-$  state has the lowest energy relative to the other states at all four of our most sophisticated ab initio levels, we are confident that the  $^4\Sigma^-$  state is the ground electronic state. Our calculated dissociation energy ( $D_e$ ) of  $\text{MgN}(^4\Sigma^-)$  is 0.50 eV at the QCISD(T)/6-311+G(2df) level.

*AIB.* The two valence isoelectronic molecules  $\text{B}_2$  and  $\text{Al}_2$  are known to have  $^3\Sigma_g^- 1.31$  and  $^3\Pi_u 32$  ground electronic states, respectively. However, the  $\text{B}_2$  molecule has a very low-lying  $^5\Sigma_u^-$  first excited state ( $T_e = 1701 \text{ cm}^{-1}$ <sup>31</sup>) and  $\text{Al}_2$  has a low-lying  $^3\Sigma_g^-$  first excited state ( $T_e = 200 \text{ cm}^{-1}$ <sup>32</sup>). Therefore, for AIB we anticipate that one of the  $^3\Pi_r$  ( $1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$ ),  $^5\Sigma^-$  ( $1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$ ), or  $^3\Sigma^-$  ( $1\sigma^2 2\sigma^2 1\pi^2$ ) states will be the ground state, while the others are low-lying excited states. We carried out calculations on states of these three symmetries at several levels of theory (Table 8).

At the MP2(full)/6-311+G\* level, the  $^3\Pi_r$  state is the lowest with the  $^3\Sigma^-$  the first and the  $^5\Sigma^-$  the second excited states. We find the same ordering at the PMP4 and QCISD(T) levels; however, at the QCISD(T)/6-311+G(2df) level, the energy difference between the  $^3\Pi_r$  and  $^3\Sigma^-$  states is only 0.2 kcal/mol.

The  $^5\Sigma^-$  second excited state is higher in energy by 22.6 kcal/mol and, therefore, is not a candidate for the ground electronic state of AIB. Although the  $^3\Pi_r$  state is lowest at all levels of theory, the spin contamination of the  $^3\Sigma^-$  state is very high. Because these states have very nearly identical total energies at both the PMP4 and QCISD(T) levels, we are not able to predict with certainty the ground electronic state from these data. Therefore, we studied these states again at the MCSCF and CASSCF-MRCISD(Q) levels of theory.

MCSCF calculations have been performed using six valence electrons in eight valence active MOs (giving 1512 CSFs). The three lowest triplet roots were then calculated using the state-averaged (SA) MCSCF methodology. The optimized bond lengths for the  $^3\Pi_r$  and  $^3\Sigma^-$  states at this level are very close to the those at the QCISD(T) level, while the MCSCF harmonic frequencies are both lower than at the MP2(full)/6-311+G\* level. The  $^3\Sigma^-$  state is the lowest at MCSCF level, and the  $^3\Pi_r$  is the first excited lying 2.6 kcal/mol higher. This ordering contradicts all of our previous results. Although these MCSCF calculations have no spin contamination and all important valence orbitals are included in variational calculation, the fraction of the total correlation energy included at the MCSCF level is not high. Therefore, we examined these two states at

**TABLE 10: Calculated Molecular Properties of the Lowest MgAl States**

MgAl( $^2\Pi_r$ )	MgAl( $^2\Sigma^+$ )	MgAl( $^4\Pi_r$ )	MgAl( $^4\Sigma^-$ )	MgAl( $^2\Pi_i$ )
$1\sigma^22\sigma^21\pi^1$	$1\sigma^22\sigma^23\sigma^1$	$1\sigma^22\sigma^11\pi^13\sigma^1$	$1\sigma^22\sigma^11\pi^2$	$1\sigma^22\sigma^01\pi^3$
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
$E_{MP2} = -441.79210$	$E_{MP2} = -441.78656$	$E_{MP2} = -441.75046$	$E_{MP2} = -441.74572$	$E_{MP2} = -441.61817$
$R_e(\text{Mg-Al}) = 2.922 \text{ \AA}$	$R_e(\text{Mg-Al}) = 3.327 \text{ \AA}$	$R_e(\text{Mg-Al}) = 2.723 \text{ \AA}$	$R_e(\text{Mg-Al}) = 2.484 \text{ \AA}$	$R_e(\text{Mg-Al}) = 2.355 \text{ \AA}$
$\omega_e = 192 \text{ cm}^{-1}$	$\omega_e = 95 \text{ cm}^{-1}$	$\omega_e = 297 \text{ cm}^{-1}$	$\omega_e = 213 \text{ cm}^{-1}$	$\omega_e = 361 \text{ cm}^{-1}$
$\langle S^2 \rangle = 0.781$	$\langle S^2 \rangle = 0.848$	$\langle S^2 \rangle = 3.758$	$\langle S^2 \rangle = 3.859$	$\langle S^2 \rangle = 1.732$
MCSCF//MCSCF	MCSCF//MCSCF			
$R(\text{Mg-Al}) = 3.03 \text{ \AA}$	$R(\text{Mg-Al}) = 3.22 \text{ \AA}$			
$\omega_e = 131 \text{ cm}^{-1}$	$\omega_e = 178 \text{ cm}^{-1}$			
$E_{MCSCF} = -441.53167$	$E_{MCSCF} = -441.50779$			
$T_e = 0.0 \text{ kcal/mol}$	$T_e = 15.0 \text{ kcal/mol}$			
QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)
//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//QCISD(T)/6-311+G(2df)	//MP2(full)/6-311+G*
$R_e(\text{Mg-Al}) = 2.901 \text{ \AA}$	$R_e(\text{Mg-Al}) = 3.269 \text{ \AA}$	$R_e(\text{Mg-Al}) = 2.750 \text{ \AA}$	$R_e(\text{Mg-Al}) = 2.536 \text{ \AA}$	$R_e(\text{Mg-Al}) = 2.355 \text{ \AA}$
$E_{PMP4} = -441.57492$	$E_{PMP4} = -441.56902$	$E_{PMP4} = -441.52757$	$E_{PMP4} = -441.52570$	$E_{PMP4} = -441.40985$
$E_{QCISD(T)} = -441.57843$	$E_{QCISD(T)} = -441.57131$	$E_{QCISD(T)} = -441.52980$	$E_{QCISD(T)} = -441.53089$	$E_{QCISD(T)} = -441.42436$
$T_{ePMP4} = 0.0 \text{ kcal/mol}$	$T_{ePMP4} = 3.7 \text{ kcal/mol}$	$T_{ePMP4} = 29.7 \text{ kcal/mol}$	$T_{ePMP4} = 30.9 \text{ kcal/mol}$	$T_{ePMP4} = 103.6 \text{ kcal/mol}$
$T_{eQCISD(T)} = 0.0 \text{ kcal/mol}$	$T_{eQCISD(T)} = 4.5 \text{ kcal/mol}$	$T_{eQCISD(T)} = 30.5 \text{ kcal/mol}$	$T_{eQCISD(T)} = 29.8 \text{ kcal/mol}$	$T_{eQCISD(T)} = 96.7 \text{ kcal/mol}$

the CASSCF–MRCISD(Q) level using a  $(17s12p5d4f/7s5p3d2f)_{Al} + (14s9p4d3f/7s5p3d2f)_B$  basis set. The CASSCF expansion included 378 ( $^3\Sigma^-$ ) and 384 ( $^3\Pi_r$ ) configurations, which represent all possible distribution of six valence electrons in  $(3,2,2,1)$  active orbitals. All single and double excitations from these 378 ( $^3\Sigma^-$ ) and 384 ( $^3\Pi_r$ ) CASSCF configurations were then included in the MRCISD calculations giving 1 555 606 ( $^3\Sigma^-$ ) and 1 154 220 ( $^3\Pi_r$ ) MRCISD configurations. Results of these calculations are presented in Table 8.

The  $^3\Sigma^-$  state is predicted to be most stable at both the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels. The  $^3\Sigma^- \rightarrow ^3\Pi_r$  excitation energy is 2.4 kcal/mol (CASSCF–MRCISD) and 1.6 kcal/mol (CASSCF–MRCISD(Q)), which agree well with the MCSCF results. Both the  $^3\Sigma^-$  and  $^3\Pi_r$  states are well represented by Hartree–Fock wave functions  $C_{HF}(1\sigma^22\sigma^23\sigma^01\pi_x^\alpha1\pi_y^\alpha) = 0.8952$  for  $^3\Sigma^-$  and  $C_{HF}(1\sigma^22\sigma^23\sigma^0\alpha1\pi_x^\alpha) = 0.9061$  for  $^3\Pi_r$  at the optimal bond lengths. From more than 1 000 000 configurations in the MRCISD expansions, only one non-Hartree–Fock configuration has a coefficient ( $C(1\sigma^22\sigma^0-3\sigma^21\pi_x^11\pi_y^1) = 0.1985$  for  $^3\Sigma^-$ ) larger than 0.15. Moreover, the Davidson correction is small, and therefore the results at the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels are similar. The occupancies of the natural MOs for the  $^3\Sigma^-$  and  $^3\Pi_r$  states are  $1\sigma^{1.92}2\sigma^{1.78}3\sigma^{0.16}4\sigma^{0.02}1\pi_x^{0.96}1\pi_y^{0.96}2\pi_x^{0.06}2\pi_y^{0.06}$  and  $1\sigma^{1.92}2\sigma^{1.85}3\sigma^{0.99}4\sigma^{0.03}1\pi_x^{0.97}1\pi_y^{0.06}2\pi_x^{0.06}2\pi_y^{0.03}$ , respectively.

We are confident that  $^3\Sigma^-$  is the ground electronic state for AIB because (i) the results are the same at the MCSCF and CASSCF–MRCISD(Q) levels of theory, (ii)  $B_2$  has a  $^3\Sigma_g^-$  ground electronic state with a  $1701 \text{ cm}^{-1}$  excitation energy into  $^3\Pi_u$  state, and (iii) in  $Al_2$  the  $^3\Sigma_g^-$  state is located only  $200 \text{ cm}^{-1}$  above the  $^3\Pi_u$  state.<sup>32</sup> Therefore, we expect that in AIB the energy difference between these two states should be somewhere in between. Our calculated dissociation energy ( $D_e$ ) of AIB( $^3\Sigma^-$ ) is 1.78 eV at the QCISD(T)/6-311+G(2df) level.

*NaAl.* In previous work on LiB, NaB, and LiAl, three states of symmetries  $^1\Sigma^+$  ( $1\sigma^22\sigma^2$ ),  $^3\Sigma^-$  ( $1\sigma^21\pi^2$ ), and  $^3\Pi_r$  ( $1\sigma^21\pi^12\sigma^1$ ) were found to be low lying. In LiB and NaB,  $^3\Pi_r$  is the ground state while, for the valence isoelectronic LiAl, the  $^1\Sigma^+$  state is the lowest. We examined these three low-lying states for NaAl. As in the LiAl molecule, we found that the *low-spin*  $^1\Sigma^+$  state is the most stable for NaAl. However, the high-spin  $^3\Pi_r$  state is only 5.2 kcal/mol above the ground state at the QCISD(T)/6-311+G(2df) level, and the  $^3\Sigma^-$  state lies above the  $^1\Sigma^+$  state by 22.4 kcal/mol. The dissociation energy ( $D_e$ ) of NaAl( $^1\Sigma^+$ ) is predicted to be 17.8 kcal/mol at the QCISD(T)/6-311+G-

(2df) level. The energy difference between the  $^1\Sigma^+$  and  $^3\Pi_r$  states for valence isoelectronic LiAl was studied at the CASSCF–MRCISD(Q) level using a  $(17s12p5d4f/7s5p3d2f)_{Al} + (14s9p4d3f/7s5p3d2f)_Li$  basis set (see below), and we obtained a very good agreement between QCISD(T) and CASSCF–MRCISD(Q) level results for the  $^3\Pi_r \leftarrow ^1\Sigma^+$  excitation energy. Because the energy differences between the  $^1\Sigma^+$  and  $^3\Pi_r$  states for LiAl and NaAl are the same, we are confident that our prediction of the  $^1\Sigma^+$  ground electronic state for NaAl is reliable.

*MgAl.* This molecule is valence isoelectronic to BeB, so we studied the same five low-lying electronic states:  $^2\Pi_r$  ( $1\sigma^22\sigma^21\pi^1$ ),  $^2\Sigma^+$  ( $1\sigma^22\sigma^23\sigma^1$ ),  $^4\Pi_r$  ( $1\sigma^22\sigma^11\pi^13\sigma^1$ ),  $^4\Sigma^-$  ( $1\sigma^22\sigma^11\pi^2$ ), and  $^2\Pi_i$  ( $1\sigma^21\pi^3$ ) as we identified for BeB. Preliminary calculations at the MP2(full)/6-311+G\* level were carried out for  $^2\Pi_r$ ,  $^2\Sigma^+$ ,  $^4\Pi_r$ ,  $^4\Sigma^-$ , and  $^2\Pi_i$  states. We found the  $^2\Pi_r$  state to be the lowest (Table 10). Using a more sophisticated correlation method (QCISD(T)/6-311+G(2df)), the  $^2\Sigma^+$  first excited state is found to be only 4.5 kcal/mol above the ground  $^2\Pi_r$  state. Therefore, we studied these two lowest states at the MCSCF level of theory.

The MCSCF calculations were performed using five valence electrons in eight valence MOs, which gave rise to 1512 CSFs. The three lowest doublet roots were calculated using the SA MCSCF methodology. The  $^2\Pi_r$  state was also found to be lowest at the MCSCF level. The  $^2\Sigma^+$  state is higher in energy by 15.0 kcal/mol. Thus, for MgAl we are confident that the  $^2\Pi_r$  state is the ground electronic state because (i) the two low-lying states have small spin contaminations, (ii) the ground electronic state is the same at the PMP4, QCISD(T), and MCSCF levels, and (iii) the relative energy range between PMP4 and QCISD(T) is only 0.8 kcal/mol, less than the first excitation energy. Our calculated dissociation energy ( $D_e$ ) of MgAl ( $^2\Pi_r$ ) is 0.34 eV at the QCISD(T)/6-311+G(2df) level.

In summary, we have identified the ground electronic states of 10 molecules that, as yet, are theoretically and experimentally uncharacterized. In the following section, we present results of our current calculations on five other molecules which were studied before—LiAl, BeP, BP, MgSi, and SiP—but for which the ground electronic states have not been determined with certainty.

#### B. Five Diatomics Whose Ground States Are Uncertain.

*LiAl.* In our previous work<sup>10c</sup> we studied three  $^1\Sigma^+$  ( $1\sigma^22\sigma^2$ ),  $^3\Sigma^-$  ( $1\sigma^21\pi^2$ ), and  $^3\Pi_r$  ( $1\sigma^21\pi^12\sigma^1$ ) low-lying states of LiAl (Table 11) and found the low-spin  $^1\Sigma^+$  state to be the most stable. However, the lowest high-spin  $^3\Pi_r$  state is predicted to be only 5.1 kcal/mol higher at the QCISD(T)/6-311+G\* level, and the  $^3\Sigma^-$  state lies only 21.2 kcal/mol above the  $^1\Sigma^+$ . Our calculated dissociation energy for LiAl( $^1\Sigma^+$ ) was 23.3 kcal/mol.



**TABLE 11: Calculated Molecular Properties of the Lowest LiAl States**

LiAl( $^1\Sigma^+$ )	LiAl( $^3\Pi_r$ )
$1\sigma^22\sigma^2$	$1\sigma^22\sigma^11\pi^1$
CASSCF–MRCISD	CASSCF–MRCISD
$R_e(\text{Li–Al}) = 2.858 \text{ \AA}$	$R_e(\text{Li–Al}) = 2.650 \text{ \AA}$
$\omega_e = 312 \text{ cm}^{-1}$	$\omega_e = 339 \text{ cm}^{-1}$
$E_{\text{CASSCF–MRCISD}} = -249.40427$	$E_{\text{CASSCF–MRCISD}} = -249.39614$
$T_{e\text{CASSCF–MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF–MRCISD}} = 5.1 \text{ kcal/mol}$
CASSCF–MRCISD(Q)	CASSCF–MRCISD(Q)
$R_e(\text{Li–Al}) = 2.859 \text{ \AA}$	$R_e(\text{Li–Al}) = 2.649 \text{ \AA}$
$\omega_e = 310 \text{ cm}^{-1}$	$\omega_e = 339 \text{ cm}^{-1}$
$E_{\text{CASSCF–MRCISD(Q)}} = -249.40479$	$E_{\text{CASSCF–MRCISD(Q)}} = -249.39685$
$T_{e\text{CASSCF–MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF–MRCISD(Q)}} = 5.0 \text{ kcal/mol}$

Because the energy difference between the  $^1\Sigma^+$  and  $^3\Pi_r$  states is small, we performed calculations on these two states at the CASSCF–MRCISD(Q) level using  $(17s12p5d4f/7s5p3d2f)_{\text{Al}} + (14s9p4d3f/7s5p3d2f)_{\text{Li}}$  basis sets. The CASSCF expansion included 152 ( $^1\Sigma^+$ ) and 160 ( $^3\Pi_r$ ) configurations, which represent all possible distributions of the valence electrons among (4,2,2,1) active orbitals. All single and double excitations from these CASSCF configurations were then included in our MRCISD calculations, giving 84 149 ( $^1\Sigma^+$ ) and 117 475 ( $^3\Pi_r$ ) MRCISD configurations. The Davidson correction to the MRCISD energy was very small for both states, so our results at the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels are very similar (Table 11).

The  $^1\Sigma^+$  state is found to be the most stable at both the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels, with the  $^3\Pi_r$  state higher in energy by 5.0 kcal/mol. This is the same excitation energy we found at the QCISD(T) level, so we are confident that  $^1\Sigma^+$  is the ground electronic state for LiAl. Both the  $^3\Pi_r$  and  $^1\Sigma^+$  states are well represented by Hartree–Fock wave functions ( $C_{\text{HF}}(1\sigma^22\sigma^2) = 0.9163$  for  $^1\Sigma^+$  and  $C_{\text{HF}}(1\sigma^22\sigma^11\pi_x^\alpha) = 0.9476$  for  $^3\Pi_r$ ). Among all configurations in the MRCISD expansions for both these configurations, only one configuration has a coefficient ( $C(1\sigma^22\sigma^03\sigma^2) = -0.1656$  for  $^1\Sigma^+$ ) larger than 0.15. The occupancies of the natural MO for the  $^1\Sigma^+$  and  $^3\Pi_r$  states are  $1\sigma^{1.88}2\sigma^{1.78}3\sigma^{0.08}1\pi_x^{0.08}1\pi_y^{0.08}2\pi_x^{0.03}2\pi_y^{0.03}$  and  $1\sigma^{1.88}2\sigma^{0.98}3\sigma^{0.02}1\pi_x^{0.97}1\pi_y^{0.05}2\pi_x^{0.03}2\pi_y^{0.01}$ , respectively.

**MgSi.** In our previous work<sup>11b</sup> we studied five  $^1\Sigma^+$  ( $1\sigma^21\pi^4$ ),  $^3\Sigma^-$  ( $1\sigma^22\sigma^11\pi^2$ ),  $^3\Pi_r$  ( $1\sigma^22\sigma^11\pi^13\sigma^1$ ),  $^3\Pi_i$  ( $1\sigma^22\sigma^11\pi^3$ ), and  $^5\Sigma^-$  ( $1\sigma^22\sigma^11\pi^23\sigma^1$ ) electronic states of the MgSi molecule, and we found the  $^3\Sigma^-$  state to be the most stable. However, the high-spin  $^3\Pi_r$  state is only 2.7 kcal/mol less stable at the PMP4/6-311+G\* level. Because the energy difference between the  $^3\Sigma^-$  and  $^3\Pi_r$  states is small, we carried out calculations on these two states at the CASSCF–MRCISD(Q) level using  $(17s12p5d4f/7s5p3d2f)_{\text{Mg,Si}}$  basis sets. The CASSCF expansion included 378 ( $^3\Sigma^-$ ) and 384 ( $^3\Pi_r$ ) configurations, which represent all possible distributions of the valence electron among (3,2,2,1) active orbitals. All single and double excitations from these CASSCF configurations were then included in the MRCISD calculations giving 1 054 150 ( $^3\Sigma^-$ ) and 1 052 968 ( $^3\Pi_r$ ) MRCISD configurations. The Davidson correction to the MRCISD energy was very small for both states as a result of which results at the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels are very close to each other (Table 12).

The  $^3\Sigma^-$  state is predicted to be the most stable at both the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels, and the  $^3\Pi_r$  state is higher in energy by 16–18 kcal/mol. Therefore, we are confident in suggesting that  $^3\Sigma^-$  is the ground electronic state for MgSi. Both the  $^3\Pi_r$  and  $^3\Sigma^-$  states are quite well represented by a Hartree–Fock wave function ( $C_{\text{HF}}(1\sigma^22\sigma^2$

**TABLE 12: Calculated Molecular Properties of the Lowest MgSi States**

MgSi( $^3\Sigma^-$ )	MgSi( $^3\Pi_r$ )
$1\sigma^22\sigma^11\pi^2$	$1\sigma^22\sigma^11\pi^13\sigma^1$
CASSCF–MRCISD	CASSCF–MRCISD
$R_e(\text{Mg–Si}) = 2.556 \text{ \AA}$	$R_e(\text{Mg–Si}) = 2.768 \text{ \AA}$
$\omega_e = 317 \text{ cm}^{-1}$	$\omega_e = 271 \text{ cm}^{-1}$
$E_{\text{CASSCF–MRCISD}} = -488.62011$	$E_{\text{CASSCF–MRCISD}} = -488.59148$
$T_{e\text{CASSCF–MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF–MRCISD}} = 18.0 \text{ kcal/mol}$
CASSCF–MRCISD(Q)	CASSCF–MRCISD(Q)
$R_e(\text{Mg–Si}) = 2.559 \text{ \AA}$	$R_e(\text{Mg–Si}) = 2.876 \text{ \AA}$
$\omega_e = 314 \text{ cm}^{-1}$	$\omega_e = 264 \text{ cm}^{-1}$
$E_{\text{CASSCF–MRCISD(Q)}} = -488.62663$	$E_{\text{CASSCF–MRCISD(Q)}} = -488.60041$
$T_{e\text{CASSCF–MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF–MRCISD(Q)}} = 16.5 \text{ kcal/mol}$

**TABLE 13: Calculated Molecular Properties of the Lowest BeP States**

BeP( $^4\Sigma^-$ )	BeP( $^2\Pi_i$ )
$1\sigma^22\sigma^11\pi^23\sigma^1$	$1\sigma^22\sigma^11\pi^3$
CASSCF–MRCISD	CASSCF–MRCISD
$R_e(\text{Be–P}) = 2.063 \text{ \AA}$	$R_e(\text{Be–P}) = 1.924 \text{ \AA}$
$\omega_e = 627 \text{ cm}^{-1}$	$\omega_e = 778 \text{ cm}^{-1}$
$E_{\text{CASSCF–MRCISD}} = -355.47841$	$E_{\text{CASSCF–MRCISD}} = -355.47367$
$T_{e\text{CASSCF–MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF–MRCISD}} = 3.0 \text{ kcal/mol}$
CASSCF–MRCISD(Q)	CASSCF–MRCISD(Q)
$R_e(\text{Be–P}) = 2.082 \text{ \AA}$	$R_e(\text{Be–P}) = 1.927 \text{ \AA}$
$\omega_e = 586 \text{ cm}^{-1}$	$\omega_e = 770 \text{ cm}^{-1}$
$E_{\text{CASSCF–MRCISD(Q)}} = -355.49071$	$E_{\text{CASSCF–MRCISD(Q)}} = -355.48606$
$T_{e\text{CASSCF–MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{e\text{CASSCF–MRCISD(Q)}} = 2.9 \text{ kcal/mol}$

$3\sigma^11\pi_x^1) = 0.9035$  for  $^3\Pi_r$  and  $C_{\text{HF}}(1\sigma^22\sigma^11\pi_x^\alpha1\pi_y^\alpha) = 0.8851$  for  $^3\Sigma^-$ ). Among all of the configurations in the MRCISD expansions for both these configurations, the only configuration with a coefficient larger than 0.15 is ( $C(1\sigma^22\sigma^03\sigma^21\pi_x^\alpha1\pi_y^\alpha) = -0.2459$  for  $^3\Sigma^-$ ). The occupancies of the natural MO for the  $^3\Sigma^-$  and  $^3\Pi_r$  states are  $1\sigma^{1.92}2\sigma^{1.75}3\sigma^{0.21}4\sigma^{0.02}1\pi_x^{0.97}1\pi_y^{0.97}2\pi_x^{0.03}2\pi_y^{0.03}$  and  $1\sigma^{1.91}2\sigma^{1.86}3\sigma^{0.98}4\sigma^{0.04}1\pi_x^{0.98}1\pi_y^{0.07}2\pi_x^{0.04}2\pi_y^{0.03}$ , respectively.

**BeP.** In our previous study<sup>14</sup> we found two electronic states,  $^4\Sigma^-$  ( $1\sigma^22\sigma^11\pi^23\sigma^1$ ) and  $^2\Pi_i$  ( $1\sigma^22\sigma^11\pi^3$ ), to be the most stable for BeP. At the PMP4/6-311+G(2df) and at QCISD(T)/6-311+G(2df) levels, the  $^4\Sigma^-$  state is lower by only 3.1 and 3.5 kcal/mol, respectively. Calculations on these two states at the CASSCF–MRCISD(Q) level using a  $(17s12p5d4f/7s5p3d2f)_{\text{P}} + (14s9p4d3f/7s5p3d2f)_{\text{Be}}$  basis set produced expansions with 104 ( $^4\Sigma^-$ ) and 196 ( $^2\Pi_i$ ) configurations, which represent all possible distributions of seven valence electrons in (3,2,2,0) active orbitals. All single and double excitations from these CASSCF configurations were then included in MRCISD calculations giving 955 575 ( $^4\Sigma^-$ ) and 1 204 664 ( $^2\Pi_i$ ) configurations. The Davidson correction to the MRCISD energy was modest for both states, so results at the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels are reasonably similar (Table 13).

The  $^4\Sigma^-$  state is found to be the most stable at both the CASSCF–MRCISD and CASSCF–MRCISD(Q) levels. Because this state is the ground electronic state at our four most sophisticated ab initio methods (PMP4, QCISD(T), CASSCF–MRCISD, and CASSCF–MRCISD(Q)), we are confident that  $^4\Sigma^-$  is the ground electronic state for BeP.

Both the  $^4\Sigma^-$  and  $^2\Pi_i$  states are well represented by Hartree–Fock wave functions ( $C_{\text{HF}}(1\sigma^22\sigma^23\sigma^\alpha1\pi_x^\alpha1\pi_y^\alpha) = 0.9437$  for  $^4\Sigma^-$  and  $C_{\text{HF}}(1\sigma^22\sigma^11\pi_x^\alpha1\pi_y^\alpha) = 0.9098$  for  $^2\Pi_i$ ). Among all of the configurations in the MRCISD expansions for both these states, only the Hartree–Fock configurations have coefficients larger than 0.15. The occupancies of the natural MO for the  $^4\Sigma^-$  and  $^2\Pi_i$  states are  $1\sigma^{1.95}2\sigma^{1.92}3\sigma^{0.99}4\sigma^{0.03}1\pi_x^{0.99}1\pi_y^{0.99}2\pi_x^{0.03}2\pi_y^{0.03}$  and  $1\sigma^{1.95}2\sigma^{1.85}3\sigma^{0.10}4\sigma^{0.02}1\pi_x^{0.97}1\pi_y^{1.88}2\pi_x^{0.04}2\pi_y^{0.08}$ , respectively.

	H	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl
H	H <sub>2</sub> 1 $\Sigma_g^+$														
Li	LiH 1 $\Sigma^+$	Li <sub>2</sub> 1 $\Sigma_g^+$													
Be	BeH 2 $\Sigma^+$	BeLi 2 $\Sigma^+$	Be <sub>2</sub> 1 $\Sigma_g^+$												
B	BH 1 $\Sigma^+$	B <sub>2</sub> 3 $\Pi_r$	BBe 2 $\Pi_r$	B <sub>2</sub> 3 $\Sigma_g^-$											
C	CH 2 $\Pi_r$	CLi 4 $\Sigma^-$	CBe 3 $\Sigma^-$	CB 4 $\Sigma^-$	C <sub>2</sub> 1 $\Sigma_g^+$										
N	NH 3 $\Sigma^-$	NLi 3 $\Sigma^-$	NBe 4 $\Sigma^-$	NB 3 $\Pi_i$	NC 2 $\Sigma^+$	N <sub>2</sub> 1 $\Sigma_g^+$									
O	OH 2 $\Pi_i$	OLi 2 $\Pi_i$	OBe 1 $\Sigma^+$	OB 2 $\Sigma^+$	OC 1 $\Sigma^+$	ON 2 $\Pi_r$	O <sub>2</sub> 3 $\Sigma_g^-$								
F	FH 1 $\Sigma^+$	FLi 1 $\Sigma^+$	FBe 2 $\Sigma^+$	FB 1 $\Sigma^+$	FC 2 $\Pi_r$	FN 3 $\Sigma^-$	FO 2 $\Pi_i$	F <sub>2</sub> 1 $\Sigma_g^+$							
Na	NaH 1 $\Sigma^+$	NaLi 1 $\Sigma^+$	NaBe 2 $\Sigma^+$	NaB 3 $\Pi_r$	NaC 4 $\Sigma^-$	NaN 3 $\Sigma^-$	NaO 2 $\Pi_i$	NaF 1 $\Sigma^+$	Na <sub>2</sub> 1 $\Sigma_g^+$						
Mg	MgH 2 $\Sigma^+$	MgLi 2 $\Sigma^+$	MgBe 1 $\Sigma^+$	MgB 2 $\Pi_r$	MgC 3 $\Sigma^-$	MgN 4 $\Sigma^-$	MgO 1 $\Sigma^+$	MgF 2 $\Sigma^+$	MgNa 2 $\Sigma^+$	Mg <sub>2</sub> 1 $\Sigma_g^+$					
Al	AlH 1 $\Sigma^+$	AlLi 1 $\Sigma^+$	AlBe 2 $\Pi_r$	AlB 3 $\Sigma^-$	AlC 4 $\Sigma^-$	AlN 3 $\Pi_i$	AlO 2 $\Sigma^+$	AlF 1 $\Sigma^+$	AlNa 1 $\Sigma^+$	AlMg 2 $\Pi_r$	Al <sub>2</sub> 3 $\Pi_u$				
Si	SiH 2 $\Pi_r$	SiLi 4 $\Sigma^-$	SiBe 3 $\Sigma^-$	SiB 4 $\Sigma^-$	SiC 3 $\Pi_i$	SiN 2 $\Sigma^+$	SiO 1 $\Sigma^+$	SiF 2 $\Pi_r$	SiNa 4 $\Sigma^-$	SiMg 3 $\Sigma^-$	SiAl 4 $\Sigma^-$	Si <sub>2</sub> 3 $\Sigma_g^-$			
P	PH 3 $\Sigma^-$	PLi 3 $\Sigma^-$	PBe 4 $\Sigma^-$	PB 3 $\Pi_i$	PC 2 $\Sigma^+$	PN 1 $\Sigma^+$	PO 2 $\Pi_r$	PF 3 $\Sigma^-$	PNa 3 $\Sigma^-$	PMg 4 $\Sigma^-$	PAI 3 $\Sigma^-$	PSi 2 $\Pi_i$	P <sub>2</sub> 1 $\Sigma_g^+$		
S	SH 2 $\Pi_i$	SLi 2 $\Pi_i$	SBe 1 $\Sigma^+$	SB 2 $\Sigma^+$	SC 1 $\Sigma^+$	SN 2 $\Pi_r$	SO 3 $\Sigma^-$	SF 2 $\Pi_i$	SNa 2 $\Pi_i$	SMg 1 $\Sigma^+$	SAI 2 $\Sigma^+$	SSi 1 $\Sigma^+$	SP 2 $\Pi_r$	S <sub>2</sub> 3 $\Sigma_g^-$	
Cl	ClH 1 $\Sigma^+$	CLi 1 $\Sigma^+$	ClBe 2 $\Sigma^+$	ClB 1 $\Sigma^+$	ClC 2 $\Pi_r$	ClN 3 $\Sigma^-$	ClO 2 $\Pi_i$	ClF 1 $\Sigma^+$	ClNa 1 $\Sigma^+$	ClMg 2 $\Sigma^+$	ClAl 1 $\Sigma^+$	ClSi 2 $\Pi_r$	CIP 3 $\Sigma^-$	CIS 2 $\Pi_i$	Cl <sub>2</sub> 1 $\Sigma_g^+$

**Figure 2.** Ground electronic states of first- and second-row atom diatomic molecules based on experimental and theoretical data. Diatomics with high-spin ground electronic states are marked in red.

**TABLE 14:** Calculated Molecular Properties of the Lowest BP States

BP(3 $\Pi_i$ )	BP(1 $\Sigma^+$ )
1 $\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$	1 $\sigma^2 2\sigma^2 1\pi^4$
CASSCF-MRCISD	CASSCF-MRCISD
$R_e(\text{B-P}) = 1.755 \text{ \AA}$	$R_e(\text{B-P}) = 1.684 \text{ \AA}$
$\omega_e = 920 \text{ cm}^{-1}$	$\omega_e = 1038 \text{ cm}^{-1}$
$E_{\text{CASSCF-MRCISD}} = -365.53221$	$E_{\text{CASSCF-MRCISD}} = -365.52083$
$T_{\text{eCASSCF-MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{\text{eCASSCF-MRCISD}} = 7.1 \text{ kcal/mol}$
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)
$R_e(\text{B-P}) = 1.765 \text{ \AA}$	$R_e(\text{B-P}) = 1.687 \text{ \AA}$
$\omega_e = 897 \text{ cm}^{-1}$	$\omega_e = 1026 \text{ cm}^{-1}$
$E_{\text{CASSCF-MRCISD(Q)}} = -365.55024$	$E_{\text{CASSCF-MRCISD(Q)}} = -365.53602$
$T_{\text{eCASSCF-MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{\text{eCASSCF-MRCISD(Q)}} = 8.9 \text{ kcal/mol}$

**BP.** Previously,<sup>14</sup> we found two low-energy electronic states 1 $\Sigma^+$  (1 $\sigma^2 2\sigma^2 1\pi^4$ ) and 3 $\Pi_i$  (1 $\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$ ) for BP. The 3 $\Pi_i$  state is lower by only 1.8 and 6.8 kcal/mol at the PMP4/6-311+G-(2df) and at QCISD(T)/6-311+G(2df) levels, respectively. We therefore carried out calculations of these two states at the CASSCF-MRCISD(Q) level using (17s12p5d4f/7s5p3d2f)<sub>p</sub> +

**TABLE 15:** Calculated Molecular Properties of the Lowest SiP States

SiP(2 $\Pi_i$ )	SiP(2 $\Sigma^+$ )
1 $\sigma^2 2\sigma^2 1\pi^3 2\sigma^2$	1 $\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$
CASSCF-MRCISD	CASSCF-MRCISD
$R_e(\text{Si-P}) = 2.092 \text{ \AA}$	$R_e(\text{Si-P}) = 2.011 \text{ \AA}$
$\omega_e = 608 \text{ cm}^{-1}$	$\omega_e = 638 \text{ cm}^{-1}$
$E_{\text{CASSCF-MRCISD}} = -629.79935$	$E_{\text{CASSCF-MRCISD}} = -629.79603$
$T_{\text{eCASSCF-MRCISD}} = 0.0 \text{ kcal/mol}$	$T_{\text{eCASSCF-MRCISD}} = 2.1 \text{ kcal/mol}$
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)
$R_e(\text{Si-P}) = 2.092 \text{ \AA}$	$R_e(\text{Si-P}) = 2.012 \text{ \AA}$
$\omega_e = 608 \text{ cm}^{-1}$	$\omega_e = 629 \text{ cm}^{-1}$
$E_{\text{CASSCF-MRCISD(Q)}} = -629.80846$	$E_{\text{CASSCF-MRCISD(Q)}} = -629.80502$
$T_{\text{eCASSCF-MRCISD(Q)}} = 0.0 \text{ kcal/mol}$	$T_{\text{eCASSCF-MRCISD(Q)}} = 2.2 \text{ kcal/mol}$

(14s9p4d3f/7s5p3d2f)<sub>B</sub> basis sets. The CASSCF expansion included 142 (1 $\Sigma^+$ ) and 150 (3 $\Pi_i$ ) configurations, which represent all possible distributions of the six valence electrons (two electrons occupy the 1 $\sigma$  MO in all cases) among the (3,2,2,0) active orbitals. All single and double excitations from these CASSCF configurations were then included in our

TABLE 16: Calculated and Experimental Ground State Dissociation Energies ( $D$ ) of Diatomic Molecules Contains First- and Second-Row Atoms

molecule	$D$ (calculated), eV	$D$ (experimental), eV	molecule	$D$ (calculated), eV	$D$ (experimental), eV
H <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.478071 <sup>a</sup>	4.478077 <sup>b</sup>	CSi, <sup>3</sup> Π <sub>i</sub>	4.4, <sup>F</sup> 4.29 <sup>f</sup>	4.64 <sup>d</sup>
HLi, <sup>1</sup> Σ <sup>+</sup>	2.415 <sup>c</sup>	2.429 <sup>d</sup>	CP, <sup>2</sup> Σ <sup>+</sup>	4.71, <sup>G</sup> 5.33 <sup>f</sup>	5.28 <sup>d</sup>
HBe, <sup>2</sup> Σ <sup>+</sup>	2.047 <sup>c</sup>	2.034 <sup>d</sup>	CS, <sup>1</sup> Σ <sup>+</sup>	7.476 <sup>c</sup>	7.355 <sup>d</sup>
HB, <sup>1</sup> Σ <sup>+</sup>	3.647 <sup>e</sup>	3.42 <sup>b</sup>	CCl, <sup>2</sup> Π <sub>r</sub>	4.16 <sup>f</sup>	3.34 <sup>d</sup>
HC, <sup>2</sup> Π <sub>r</sub>	3.443, <sup>c</sup> 3.577 <sup>e</sup>	3.465 <sup>d</sup>	N <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	9.10, <sup>w</sup> 9.83, <sup>x</sup> 9.70 <sup>f</sup>	9.90 <sup>d</sup>
HN, <sup>3</sup> Σ <sup>-</sup>	3.339, <sup>c</sup> 3.499 <sup>e</sup>	<3.47 <sup>d</sup>	NO, <sup>2</sup> Π <sub>i</sub>	6.565 <sup>c</sup>	
HO, <sup>2</sup> Π <sub>i</sub>	4.380, <sup>c</sup> 4.518 <sup>e</sup>	4.392 <sup>d</sup>	NF, <sup>3</sup> Σ <sup>-</sup>	3.30 <sup>H</sup>	3.5 <sup>d</sup>
HF, <sup>1</sup> Σ <sup>+</sup>	5.915, <sup>c</sup> 5.984 <sup>e</sup>	5.869 <sup>d</sup>	NNa, <sup>3</sup> Σ <sup>-</sup>	0.77 <sup>q</sup>	
HMg, <sup>2</sup> Σ <sup>+</sup>	1.27 <sup>f</sup>	1.34 <sup>d</sup>	NMg, <sup>4</sup> Σ <sup>-</sup>	0.5 <sup>q</sup>	
HAL, <sup>1</sup> Σ <sup>+</sup>	3.174 <sup>g</sup>	<3.06, <sup>d</sup> 3.170 <sup>g</sup>	NAI, <sup>3</sup> Π	2.35 <sup>i</sup>	
HSi, <sup>2</sup> Π <sub>r</sub>	3.161 <sup>g</sup>	3.06, <sup>d</sup> 3.161 <sup>g</sup>	NSi, <sup>2</sup> Σ <sup>+</sup>	3.84 <sup>G</sup>	
HP, <sup>3</sup> Σ <sup>-</sup>	3.135 <sup>g</sup>	3.122 <sup>g</sup>	NP, <sup>1</sup> Σ <sup>+</sup>	5.35 <sup>G</sup>	6.36 <sup>d</sup>
HS, <sup>2</sup> Π <sub>i</sub>	3.721 <sup>g</sup>	3.55, <sup>d</sup> 3.764 <sup>g</sup>	NS, <sup>2</sup> Π	4.69 <sup>f</sup>	
HCl, <sup>1</sup> Σ <sup>+</sup>	4.653 <sup>g</sup>	4.434, <sup>d</sup> 4.653 <sup>g</sup>	NCl, <sup>3</sup> Σ <sup>-</sup>	2.52 <sup>j</sup>	4.8 <sup>d</sup>
Li <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.02, 1.140 <sup>c</sup>	1.046 <sup>d</sup>	O <sub>2</sub> , <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	5.026, <sup>c</sup> 5.08 <sup>w</sup>	5.23 <sup>d</sup>
LiBe, <sup>2</sup> Σ <sup>+</sup>	0.26, <sup>h</sup> 0.29, <sup>i</sup> 0.25 <sup>j</sup>		OF, <sup>2</sup> Π	2.10 <sup>K</sup>	2.23 <sup>d</sup>
LiB, <sup>3</sup> Π	1.18, <sup>h</sup> 1.11 <sup>k</sup>		ONa, <sup>2</sup> Π	2.83 <sup>i</sup>	2.60 <sup>d</sup>
LiC, <sup>4</sup> Σ <sup>-</sup>	2.58 <sup>h</sup>		OMg, <sup>1</sup> Σ <sup>+</sup>	2.75 <sup>i</sup>	
LiN, <sup>3</sup> Σ <sup>-</sup>	1.49, <sup>h</sup> 1.61 <sup>f</sup>		OAl, <sup>2</sup> Σ <sup>+</sup>	4.12 <sup>L</sup>	5.27 <sup>d</sup>
LiO, <sup>2</sup> Π <sub>i</sub>	3.48, <sup>h</sup> 3.78, <sup>i</sup> 3.30 <sup>f</sup>	3.49 <sup>d</sup>	OSi, <sup>1</sup> Σ <sup>+</sup>	8.308 <sup>c</sup>	
LiF, <sup>1</sup> Σ <sup>+</sup>	5.81, <sup>h</sup> 5.980, <sup>c</sup> 6.06 <sup>i</sup>	5.91 <sup>d</sup>	OP, <sup>2</sup> Π <sub>r</sub>	6.01 <sup>M</sup>	6.15 <sup>d</sup>
LiNa, <sup>1</sup> Σ <sup>+</sup>	0.85 <sup>h</sup>	0.90 <sup>d</sup>	OS, <sup>3</sup> Σ <sup>-</sup>	5.269, <sup>c</sup> 5.29 <sup>j</sup>	5.359 <sup>d</sup>
LiMg, <sup>2</sup> Σ <sup>+</sup>	0.18, <sup>h</sup> 0.20 <sup>i</sup>		OCl, <sup>2</sup> Π	2.689 <sup>c</sup>	2.751 <sup>d</sup>
LiAl, <sup>1</sup> Σ <sup>+</sup>	1.01 <sup>h</sup>		F <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.613, <sup>c</sup> 1.518 <sup>w</sup>	1.602 <sup>d</sup>
LiSi, <sup>4</sup> Σ <sup>-</sup>	1.83 <sup>h</sup>	1.54 <sup>m</sup>	FNa, <sup>1</sup> Σ <sup>+</sup>	5.00, <sup>i</sup> 4.97 <sup>f</sup>	5.33 <sup>d</sup>
LiP, <sup>3</sup> Σ <sup>-</sup>	1.66 <sup>h</sup>	2.53 <sup>n</sup>	FMg, <sup>2</sup> Σ <sup>+</sup>	4.66, <sup>i</sup> 4.56 <sup>f</sup>	4.75 <sup>d</sup>
LiS, <sup>2</sup> Π <sub>i</sub>	3.08, <sup>h</sup> 3.30 <sup>i</sup>		FAl, <sup>1</sup> Σ <sup>+</sup>	6.89, <sup>N</sup> 7.01 <sup>f</sup>	6.89 <sup>d</sup>
LiCl, <sup>1</sup> Σ <sup>+</sup>	4.76, <sup>h</sup> 4.89, <sup>i</sup> 4.86 <sup>f</sup>	4.84 <sup>d</sup>	FSi, <sup>2</sup> Π <sub>r</sub>	6.01 <sup>f</sup>	5.57 <sup>d</sup>
Be <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.09, <sup>i</sup> 0.08–0.10 <sup>o</sup>	0.10 <sup>o</sup>	FS, <sup>3</sup> Σ <sup>-</sup>	4.47, <sup>j</sup> 4.56 <sup>f</sup>	
BeB, <sup>2</sup> Π	1.57 <sup>q</sup>		FP, <sup>2</sup> Π	3.55 <sup>f</sup>	<3.3 <sup>d</sup>
BeC, <sup>3</sup> Σ <sup>-</sup>	2.39 <sup>r</sup>		FCl, <sup>1</sup> Σ <sup>+</sup>	2.680 <sup>c</sup>	2.617 <sup>d</sup>
BeN, <sup>4</sup> Σ <sup>-</sup>	1.34 <sup>s</sup>		Na <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.850 <sup>c</sup>	0.720 <sup>d</sup>
BeO, <sup>1</sup> Σ <sup>+</sup>	4.69 <sup>f</sup>	4.60 <sup>d</sup>	NaMg, <sup>2</sup> Σ <sup>+</sup>	0.11 <sup>i</sup>	
BeF, <sup>2</sup> Σ <sup>+</sup>	5.94, <sup>i</sup> 5.71 <sup>f</sup>	5.85, <sup>d</sup> 6.26	NaAl, <sup>1</sup> Σ <sup>+</sup>	0.77 <sup>q</sup>	
BeNa, <sup>2</sup> Σ <sup>+</sup>	0.14 <sup>i</sup>		NaSi, <sup>4</sup> Σ <sup>-</sup>	1.46 <sup>u</sup>	
BeMg, <sup>1</sup> Σ <sup>+</sup>	0.008 <sup>f</sup>		NaP, <sup>3</sup> Σ <sup>-</sup>	1.21 <sup>v</sup>	
BeAl, <sup>2</sup> Π	0.40 <sup>f</sup>		NaS, <sup>2</sup> Π	2.66 <sup>i</sup>	
BeSi, <sup>3</sup> Σ <sup>-</sup>	1.28 <sup>u</sup>		NaCl, <sup>1</sup> Σ <sup>+</sup>	4.22, <sup>i</sup> 4.28 <sup>f</sup>	4.23 <sup>d</sup>
BeP, <sup>4</sup> Σ <sup>-</sup>	1.06 <sup>v</sup>		Mg <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.0575 <sup>o</sup>	0.050 <sup>d</sup>
BeS, <sup>1</sup> Σ <sup>+</sup>	2.29, <sup>i</sup> 3.23 <sup>f</sup>	3.8 <sup>d</sup>	MgAl, <sup>2</sup> Π <sub>r</sub>	0.34 <sup>q</sup>	
BeCl, <sup>2</sup> Σ <sup>+</sup>	3.87, <sup>i</sup> 3.84 <sup>f</sup>	3.99 <sup>d</sup>	MgSi, <sup>3</sup> Σ <sup>-</sup>	0.96 <sup>u</sup>	
B <sub>2</sub> , <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	2.84 <sup>w</sup>	3.02 <sup>d</sup>	MgP, <sup>4</sup> Σ <sup>-</sup>	0.54 <sup>v</sup>	
BC, <sup>4</sup> Σ <sup>-</sup>	4.21 <sup>x</sup>	4.60 <sup>d</sup>	MgS, <sup>1</sup> Σ <sup>+</sup>	1.70, <sup>i</sup> 2.23 <sup>f</sup>	<2.4 <sup>d</sup>
BN, <sup>3</sup> Π	4.56 <sup>y</sup>	3.99 <sup>z</sup>	MgCl, <sup>2</sup> Σ <sup>+</sup>	3.26, <sup>i</sup> 3.27 <sup>f</sup>	3.29 <sup>d</sup>
BO, <sup>2</sup> Σ <sup>+</sup>	8.43, <sup>A</sup> 8.32 <sup>f</sup>	8.28 <sup>d</sup>	Al <sub>2</sub> , <sup>3</sup> Π <sub>u</sub>	1.386 <sup>p</sup>	1.55 <sup>d</sup>
BF, <sup>1</sup> Σ <sup>+</sup>	7.74 <sup>B</sup>	7.81 <sup>d</sup>	AlSi, <sup>4</sup> Σ <sup>-</sup>	2.45 <sup>u</sup>	2.34 <sup>d</sup>
BNa, <sup>3</sup> Π	0.76 <sup>q</sup>		AlP, <sup>3</sup> Σ <sup>-</sup>	2.07 <sup>v</sup>	2.20 <sup>d</sup>
BMg, <sup>2</sup> Π <sub>r</sub>	0.47 <sup>q</sup>		AlS, <sup>2</sup> Σ <sup>+</sup>	3.99 <sup>R</sup>	3.84 <sup>d</sup>
BAl, <sup>3</sup> Σ <sup>-</sup>	1.78 <sup>q</sup>		AlCl, <sup>1</sup> Σ <sup>+</sup>	5.25, <sup>N</sup> 5.24 <sup>f</sup>	5.12 <sup>d</sup>
BSi, <sup>4</sup> Σ <sup>-</sup>	3.15 <sup>u</sup>	2.95 <sup>d</sup>	Si <sub>2</sub> , <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	3.213 <sup>c</sup>	3.21 <sup>d</sup>
BP, <sup>3</sup> Π	3.13 <sup>v</sup>	3.56 <sup>C</sup>	SiP, <sup>2</sup> Π <sub>i</sub>	3.35, <sup>v</sup> 3.15 <sup>G</sup>	3.73 <sup>d</sup>
BS, <sup>2</sup> Σ <sup>+</sup>	5.71 <sup>f</sup>	6.01 <sup>d</sup>	SiS, <sup>1</sup> Σ <sup>+</sup>	6.29 <sup>f</sup>	6.42 <sup>d</sup>
BCl, <sup>1</sup> Σ <sup>+</sup>	5.33, <sup>f</sup> 5.49 <sup>D</sup>	5.5 <sup>d</sup>	SiCl, <sup>2</sup> Π <sub>r</sub>	4.32 <sup>f</sup>	
C <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	6.26, <sup>w</sup> 6.40 <sup>f</sup>	6.21 <sup>d</sup>	P <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.987 <sup>c</sup>	
CN, <sup>2</sup> Σ <sup>+</sup>	7.623 <sup>c</sup>	7.76 <sup>d</sup>	PS, <sup>2</sup> Π	4.29 <sup>f</sup>	4.54 <sup>d</sup>
CO, <sup>1</sup> Σ <sup>+</sup>	11.231 <sup>c</sup>	11.092 <sup>d</sup>	PCl, <sup>3</sup> Σ <sup>-</sup>	3.19 <sup>f</sup>	
CF, <sup>2</sup> Π <sub>r</sub>	5.71 <sup>f</sup>	5.67 <sup>d</sup>	S <sub>2</sub> , <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	4.306 <sup>c</sup>	
CNa, <sup>4</sup> Σ <sup>-</sup>	1.97 <sup>q</sup>		SCL, <sup>2</sup> Π	2.78 <sup>f</sup>	
CMg, <sup>3</sup> Σ <sup>-</sup>	1.50 <sup>q</sup>		Cl <sub>2</sub> , <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.511 <sup>c</sup>	2.480 <sup>d</sup>
CAI, <sup>4</sup> Σ <sup>-</sup>	3.3 <sup>E</sup>				

<sup>a</sup> Reference 35. <sup>b</sup> Reference 36. <sup>c</sup> Reference 37. <sup>d</sup> Reference 1. <sup>e</sup> Reference 38. <sup>f</sup> Reference 39. <sup>g</sup> Reference 40. <sup>h</sup> Reference 10c. <sup>i</sup> Reference 13. <sup>j</sup> Reference 41. <sup>k</sup> Reference 10b. <sup>l</sup> Reference 42. <sup>m</sup> Reference 43. <sup>n</sup> Reference 44. <sup>o</sup> Reference 45. <sup>p</sup> Reference 46. <sup>q</sup> This work. <sup>r</sup> Reference 17. <sup>s</sup> Reference 16. <sup>t</sup> Reference 47. <sup>u</sup> Reference 11b. <sup>v</sup> Reference 14. <sup>w</sup> Reference 48. <sup>x</sup> Reference 49. <sup>y</sup> Reference 50. <sup>z</sup> Reference 51. <sup>A</sup> Reference 52. <sup>B</sup> Reference 53. <sup>C</sup> Reference 54. <sup>D</sup> Reference 55. <sup>E</sup> Reference 56. <sup>F</sup> Reference 57. <sup>G</sup> Reference 58. <sup>H</sup> Reference 59. <sup>I</sup> Reference 60. <sup>J</sup> Reference 61. <sup>K</sup> Reference 62. <sup>L</sup> Reference 63. <sup>M</sup> Reference 64. <sup>N</sup> Reference 65. <sup>O</sup> Reference 66. <sup>P</sup> Reference 67. <sup>Q</sup> Reference 68.

MRCISD calculations giving 1 089 382 (<sup>1</sup>Σ<sup>+</sup>) and 1 775 350 (<sup>3</sup>Π<sub>i</sub>) configurations. The Davidson correction to the MRCISD energy was modest as a result of which the CASSCF–MRCISD and CASSCF–MRCISD(Q) results are similar (Table 14) but not identical.

The <sup>3</sup>Π<sub>i</sub> state is predicted to be the most stable at both the

CASSCF–MRCISD and CASSCF–MRCISD(Q) levels. Because the <sup>3</sup>Π<sub>i</sub> state is the lowest at all sophisticated ab initio levels (PMP4, QCISD(T), CASSCF–MRCISD, and CASSCF–MRCISD(Q)), we are reasonably confident that <sup>3</sup>Π<sub>i</sub> is the ground state for BP.

Both the <sup>1</sup>Σ<sup>+</sup> and <sup>3</sup>Π<sub>i</sub> states are well represented by Hartree–

2	3	4	5	6	7	8	9	10	11	12	13	14
Li <sub>2</sub> 1 $\Sigma_g^+$	LiBe 2 $\Sigma^+$	LiB 3 $\Pi_r$	LiC 4 $\Sigma^-$	LiN 3 $\Sigma^-$	LiO 2 $\Pi_i$	LiF 1 $\Sigma^+$	BeF 2 $\Sigma^+$	BF 1 $\Sigma^+$	CF 2 $\Pi_r$	NF 3 $\Sigma^-$	OF 2 $\Pi_i$	F <sub>2</sub> 1 $\Sigma_g^+$
LiNa 1 $\Sigma^+$	BeNa 2 $\Sigma^+$	Be <sub>2</sub> 1 $\Sigma_g^+$	BeB 2 $\Pi_r$	BeC 3 $\Sigma^-$	BeN 4 $\Sigma^-$	BeO 1 $\Sigma^+$	BO 2 $\Sigma^+$	CO 1 $\Sigma^+$	NO 2 $\Pi_r$	O <sub>2</sub> 3 $\Sigma_g^-$	OCi 2 $\Pi_i$	FCi 1 $\Sigma^+$
Na <sub>2</sub> 1 $\Sigma_g^+$	LiMg 2 $\Sigma^+$	LiAl 1 $\Sigma^+$	LiSi 4 $\Sigma^-$	B <sub>2</sub> 3 $\Sigma_g^-$	BC 4 $\Sigma^-$	BN 3 $\Pi_i$	CN 2 $\Sigma^+$	N <sub>2</sub> 1 $\Sigma_g^+$	CCl 2 $\Pi_r$	OS 3 $\Sigma^-$	FS 2 $\Pi_i$	Cl <sub>2</sub> 1 $\Sigma_g^+$
	NaMg 2 $\Sigma^+$	BNa 3 $\Pi_r$	BeAl 2 $\Pi_r$	LiP 3 $\Sigma^-$	LiS 2 $\Pi_i$	C <sub>2</sub> 1 $\Sigma_g^+$	BeCl 2 $\Sigma^+$	BCl 1 $\Sigma^+$	NS 2 $\Pi_r$	NCl 3 $\Sigma^-$	SCl 2 $\Pi_i$	
		BeMg 1 $\Sigma^+$	BMg 2 $\Pi_r$	BeSi 3 $\Sigma^-$	BeP 4 $\Sigma^-$	LiCl 1 $\Sigma^+$	BS 2 $\Sigma^+$	CS 1 $\Sigma^+$	OP 2 $\Pi_r$	FP 3 $\Sigma^-$		
		NaAl 1 $\Sigma^+$	CNa 4 $\Sigma^-$	BAI 3 $\Sigma^-$	BSi 4 $\Sigma^-$	BeS 1 $\Sigma^+$	CP 2 $\Sigma^+$	NP 1 $\Sigma^+$	FSi 2 $\Pi_r$	PCI 3 $\Sigma^-$		
		Mg <sub>2</sub> 1 $\Sigma_g^+$	NaSi 4 $\Sigma^-$	CMg 3 $\Sigma^-$	CAI 4 $\Sigma^-$	BP 3 $\Pi_i$	NSi 2 $\Sigma^+$	OSi 1 $\Sigma^+$	SiCl 2 $\Pi_r$	S <sub>2</sub> 3 $\Sigma_g^-$		
			MgAl 2 $\Pi_r$	NNa 3 $\Sigma^-$	NMg 4 $\Sigma^-$	CSi 3 $\Pi_i$	OAl 2 $\Sigma^+$	FAI 1 $\Sigma^+$	PS 2 $\Pi_r$			
				NaP 3 $\Sigma^-$	ONa 2 $\Pi_i$	NAI 3 $\Pi_i$	FMg 2 $\Sigma^+$	AlCl 1 $\Sigma^+$				
				MgSi 3 $\Sigma^-$	NaS 2 $\Pi_i$	OMg 1 $\Sigma^+$	MgCl 2 $\Sigma^+$	SiS 1 $\Sigma^+$				
				Al <sub>2</sub> 3 $\Pi_u$	MgP 4 $\Sigma^-$	FNa 1 $\Sigma^+$	AlS 2 $\Sigma^+$	P <sub>2</sub> 1 $\Sigma_g^+$				
					AlSi 4 $\Sigma^-$	NaCl 1 $\Sigma^+$	SiP 2 $\Pi_i$					
						MgS 1 $\Sigma^+$						
						AlP 3 $\Sigma^-$						
							Si <sub>2</sub> 3 $\Sigma_g^-$					

**Figure 3.** Ground states of first- and second-row diatomic molecules viewed in terms of the number of valence electrons. High-spin exceptions are noted in red.

Fock wave functions ( $C_{HF}(1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2) = 0.8768$  for  $1\Sigma^+$  and  $C_{HF}(1\sigma^2 2\sigma^2 2\sigma^1 1\pi_x^1 1\pi_y^2) = 0.9123$  for  $3\Pi_i$ ). Among all configurations in the MRCISD expansions for both of these states, only one non-Hartree-Fock configuration ( $C(1\sigma^2 2\sigma^0 3\sigma^2 1\pi_x^2 1\pi_y^2) = -0.1654$  for  $1\Sigma^+$ ) has a coefficient larger than 0.15. The occupancies of the natural MOs for the  $1\Sigma^+$  and  $3\Pi_i$  states are  $1\sigma^{1.962} 2\sigma^{1.823} 3\sigma^{0.164} 4\sigma^{0.021} \pi_x^{1.861} \pi_y^{1.862} \pi_x^{0.112} \pi_y^{0.11}$  and  $1\sigma^{1.962} 2\sigma^{1.903} 3\sigma^{1.004} 4\sigma^{0.031} \pi_x^{0.971} \pi_y^{1.872} \pi_x^{0.062} \pi_y^{0.10}$ , respectively.

**SiP.** In our previous study<sup>14</sup> we identified two low-energy electronic states  $2\Sigma^+$  ( $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$ ) and  $2\Pi_i$  ( $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2$ ) for the SiP molecule. At the PMP4/6-311+G(2df) level, the  $2\Sigma^+$  state is lower by 3.3 kcal/mol, but at the QCISD(T)/6-311+G(2df) level, the  $2\Pi_i$  is more stable by 0.9 kcal/mol. Again, we carried out calculations of these two states at the CASSCF-MRCISD(Q) level using (17s12p5d4f/7s5p3d2f)<sub>Si,P</sub> basis sets. The CASSCF expansion included 208 ( $2\Sigma^+$ ) and 196 ( $2\Pi_i$ ) configurations, which represent all possible distributions of the seven valence electrons (two electrons occupy the  $1\sigma$  MO in all cases) among the (3,2,2,0) active orbitals. All single and double excitations from these CASSCF configurations

were then included in our MRCISD calculations giving 420 340 ( $2\Sigma^+$ ) and 416 604 ( $2\Pi_i$ ) configurations. The Davidson correction to the MRCISD energy was modest so the CASSCF-MRCISD and CASSCF-MRCISD(Q) results are in reasonably close agreement (Table 15).

The  $2\Pi_i$  state is found to be the most stable at both the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels. Because the  $2\Pi_i$  ground electronic state is lowest at these sophisticated ab initio methods (QCISD(T), CASSCF-MRCISD, and CASSCF-MRCISD(Q)), we are reasonably confident in claiming that  $2\Pi_i$  is the ground electronic state for SiP. Both the  $2\Sigma^+$  and  $2\Pi_i$  states are well represented by Hartree-Fock wave functions ( $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2) = 0.9042$  and  $2\Sigma^+$  and  $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^2) = 0.9187$  for  $2\Pi_i$ ). Among all configurations in the MRCISD expansions for both of these states, only the Hartree-Fock configurations have coefficients larger than 0.15. The occupancies of the natural MOs for the  $2\Sigma^+$  and  $2\Pi_i$  states are  $1\sigma^{2.002} 2\sigma^{1.903} 3\sigma^{1.004} 4\sigma^{0.031} \pi_x^{1.871} \pi_y^{1.872} \pi_x^{0.062} \pi_y^{0.10}$  and  $1\sigma^{2.002} 2\sigma^{1.943} 3\sigma^{1.904} 4\sigma^{0.071} \pi_x^{0.971} \pi_y^{1.872} \pi_x^{0.062} \pi_y^{0.10}$ , respectively.

## IV. Overview

In Figure 2, the term symbols of the ground electronic states calculated and experimentally determined (where known) are given for all 120 first- and second-row diatomic molecules, and in Table 16 the theoretical and available experimental dissociation energies for these ground states are presented. In Table 16 some of the experimental dissociation energies are  $D_e$  values and some are  $D_0$ . Because the differences between such values are smaller in most cases than the accuracy of our calculations, we do not emphasize these differences. Moreover, we do not cite all of the theoretical data published in the literature but select what we feel are the most reliable data.

The conventional *valence* MO ordering for first-row *homonuclear* diatomic molecules is  $1\sigma_g < 1\sigma_u < 1\pi_u < 2\sigma_g < 1\pi_g < 2\sigma_u$  for lithium to nitrogen, with the  $1\pi_u$  and  $2\sigma_g$  orbitals reversed for  $O_2$  and  $F_2$ .<sup>33</sup> From this ordering one can successfully predict the ground electronic states for all first- and second-row homonuclear diatomics, and these predictions agree with the findings given in Figure 2.

However, when heteronuclear species are considered, it is difficult to predict the order in which the valence MOs are filled, especially for the 4–8 valence electron cases. Assuming an MO ordering analogous to that found in most homonuclear cases,  $1\sigma < 2\sigma < 1\pi < 3\sigma < 2\pi < 4\sigma$ , one would predict the following ground electronic states for 2–16 valence electrons:  $^1\Sigma^+ (1\sigma^2)$ ,  $^2\Sigma^+ (1\sigma^2 2\sigma^1)$ ,  $^1\Sigma^+ (1\sigma^2 2\sigma^2)$ ,  $^2\Pi_r (1\sigma^2 2\sigma^2 1\pi^1)$ ,  $^3\Sigma^- (1\sigma^2 2\sigma^2 1\pi^2)$ ,  $^2\Pi_i (1\sigma^2 2\sigma^2 1\pi^3)$ ,  $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4)$ ,  $^2\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1)$ ,  $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2)$ ,  $^2\Pi_r (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^1)$ ,  $^3\Sigma^- (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^2)$ ,  $^2\Pi_i (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^3)$ ,  $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^4)$ ,  $^2\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^4 4\sigma^1)$ , and  $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^4 4\sigma^2)$ .

As shown in Figure 2 in green, most first- and second-row diatomic molecules have the ground electronic states that are expected based on the above MO ordering:  $H_2$ , LiH,  $Li_2$ , LiNa,  $Na_2$  ( $^1\Sigma^+ (1\sigma^2)$ ); BeH, LiBe, MgH, LiMg, NaBe, NaMg ( $^2\Sigma^+ (1\sigma^2 2\sigma^1)$ ); BH,  $Be_2$ , AlH, LiAl, BeMg, NaAl,  $Mg_2$  ( $^1\Sigma^+ (1\sigma^2 2\sigma^2)$ ); CH, BeB, SiH, BeAl, MgB, MgAl ( $^2\Pi_r (1\sigma^2 2\sigma^2 1\pi^1)$ ); NH, LiN, BeC,  $B_2$ , PH, LiP, BeSi, BAl, MgC, NaN, NaP, MgSi ( $^3\Sigma^- (1\sigma^2 2\sigma^2 1\pi^2)$ ); OH, LiO, SH, LiS, NaO, NaS ( $^2\Pi_i (1\sigma^2 2\sigma^2 1\pi^3)$ ); HF, LiF, BeO,  $C_2$ , HCl, LiCl, BeS, MgO, NaF, NaCl, MgS ( $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4)$ ); BeF, BO, CN, BeCl, BS, PC, SiN, AlO, MgF, MgCl, AlS ( $^2\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1)$ ); BF, CO,  $N_2$ , BCl, CS, PN, SiO, AlF, ClAl, SiS,  $P_2$  ( $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2)$ ); CF, NO, CCl, SN, PO, SiF, SiCl, SP ( $^2\Pi_r (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^1)$ ); NF,  $O_2$ , NCl, SO, PF, PCl,  $S_2$  ( $^3\Sigma^- (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^2)$ ); OF, ClO, SF, SCl ( $^2\Pi_i (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^3)$ ); and  $F_2$ , ClF,  $Cl_2$  ( $^1\Sigma^+ (1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^4)$ ). However, 20 diatomics (marked in red in Figure 2) do not fit the pattern and have unexpectedly high-spin ground electronic states.

The possibility for ground states with higher spin multiplicity than expected considering the Aufbau principle arises due to the near degeneracy of the  $2\sigma$  and  $1\pi$  MOs or of the  $1\pi$  and  $3\sigma$  MOs. For example, the  $1\sigma^2 2\sigma^2 1\pi^0$  states lie slightly above the corresponding  $1\sigma^2 2\sigma^2 1\pi^1$  states for LiB and NaB, and the  $1\sigma^2 2\sigma^2 1\pi^1$  states are above the  $1\sigma^2 2\sigma^2 1\pi^2$  states for LiC, NaC, LiSi, and NaSi.

Another group of high-spin ground state molecules arise because of quasi-degeneracy between the  $1\pi$  and  $3\sigma$  orbitals. For example,  $1\sigma^2 2\sigma^2 1\pi^3$  lies above  $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$  for BeN, BC, BeP, BSi, AlC, MgN, MgP, and AlSi, and  $1\sigma^2 2\sigma^2 1\pi^4$  states lie above  $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$  for BN, BP, CSi, AlN. These two groups of “peculiar” species arise when there are 4–5 or 7–8 valence electrons.

Clearly, the isoelectronic principle,<sup>34</sup> which is widely used in chemistry, does not work well for certain diatomic molecules

with 4–8 valence electrons. It appears that the Aufbau principle, using the “standard” order of MOs, works for all first- and second-row diatomics except *some* of those with 4–5 or 7–8 valence electrons. However, not all of the 4–5 or 7–8 electron cases produce high-spin (i.e.,  $2\sigma^1 1\pi^1$ ,  $2\sigma^1 1\pi^2$ ,  $1\pi^2 3\sigma^1$ , or  $1\pi^3 3\sigma^1$ ) ground states; some of the 4–5 electron cases yield  $2\sigma^2$  or  $2\sigma^2 1\pi^1$  low-spin ground states, and some of the 7–8 electron molecules produce  $1\pi^3$  or  $1\pi^4$  ground states. Inspection of Figure 3, where the low- and high-spin ground states are examined according to their number of valence electrons, reveals that when group 3, 4, and 5 elements are involved, high-spin states can be expected; group 6 and 7 elements do *not* produce high-spin ground states. We therefore note in closing that challenges remain for students of chemistry even within the realm of predicting the energy ordering for electronic states of diatomic molecules and for understanding why such orderings arise. Even greater challenges arise when considering three or larger atomic clusters especially when group 3, 4, or 5 elements are involved.

**Acknowledgment.** This work was supported by the Office of Naval Research and by NSF Grant CHE9116286. We thank Dmitry Boldyrev for assistance with the color graphics used to prepare Figures 1–3.

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