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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 twenty of the diatomics studies. The twenty 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.

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by

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PERIODICITY AND PECULIARITY IN 120 FIRST AND SECOND ROW DIATOMIC MOLECULES

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Abstract

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 twenty of the diatomics studies. The twenty 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 15x16/2=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 corresponding bond lengths (R_e) and dissociation energies (D_e) are well established. However, such is not the case; in Fig. 1 those diatomics for which even the ground electronic states have not been so characterized are displayed

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in burgundy. In purple are shown the diatomics whose ground electronic states are reasonably well characterized. Most of the experimental data used to create Fig. 1 was taken from the monograph of Huber and Herzberg,[1] although several species' properties were obtained from more recent sources.[2-9] 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.

(Figure 1 near here please)

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 thirty-three experimentally uncharacterized diatoms shown in Fig. 1 burgundy. In particular, the following twenty-three have been studied in earlier theoretical works: LiB,[10] LiC,[10c,11] LiN,[10c,12] LiMg,[13] LiAl,[10c] LiSi,[10c,11] LiP,[14] LiS,[15] BeN,[16] BeC,[17] BeNa,[13] BeAl,[13] BeSi,[11b] BeP,[14] BP,[14] NaMg,[13] NaSi,[10c] NaP,[14] NaS,[15] MgSi,[10c] MgP,[14] AlP,[14] and SiP.[14] In the present work, we

present our new results on the remaining ten diatomic molecules: BeB, NaB, NaC, NaN, MgB, MgC, MgN, AlB, NaAl and MgAl and we repeat high level calculations on several of the other twenty-three 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 Fig. 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 ten diatomics (BeB, NaB, NaC, NaN, MgB, MgC, MgN, AlB, NaAl and MgAl) for which new data is presented here were optimized using analytical gradients[18] and polarized split-valence basis sets of 6-311+G*[19] 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[20] and by the (U)QCISD(T) method[21] 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).[22] 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[23] 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 space self-consistent field - multi-reference configuration interaction method, including all single and double excitations from the reference configurations (CASSCF-MRCISD)[24-26]. In diatomic molecules treated by CASSCF and CASSCF-MRCISD calculations in C_{2v} symmetry, the first (a_1) representation contains both σ and δ orbitals, the second (b_1) and third (b_2) contain π_x and π_y orbitals, respectively, and the forth (a_2) 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.[27]. These calculations were performed using the MOLCAS-2 program.[28]

The MgAl and BAl molecules were also studied at the MCSCF level using Dunnings' augmented correlation consistent polarized valence basis sets (aug-cc-pVDZ)[29] and the GAMESS[30] 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 ten newly examined diatoms as well as for five others examined by earlier workers and reexamined here are summarized in Tables I-XV.

III. RESULTS AND DISCUSSIONS.

A. The Ten As Yet Uncharacterized Diatomics

BeB. Assuming doubly occupancy for the 1σ valence orbital, the three other valence electrons may be distributed throughout the lowest 2σ, 3σ and 1π valence orbitals giving five possible occupancies: $1\sigma^2 2\sigma^2 1\pi^1$, $1\sigma^2 2\sigma^2 3\sigma^1$, $1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$, $1\sigma^2 2\sigma^1 1\pi^2$ and $1\sigma^2 1\pi^3$, which lead to several low-lying electronic states: $^2\Pi_r$ ($1\sigma^2 2\sigma^2 1\pi^1$), $^2\Sigma^+$ ($1\sigma^2 2\sigma^2 3\sigma^1$), $^2\Pi_r$ 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 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 I). However, when larger basis sets and

(Table I near here please)

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 1σ 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 II were we find the <u>high spin</u> $^3\Pi_r$ ($1\sigma^2 2\sigma^1 1\pi^1$) state

(Table II near here please)

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 $(17s12p5d4f/7s5p3d2f)_{Na}$ + $(14s9p4d3d/7s5p3d2f)_B$ 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) level are very close to each other (Table II). 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 ($C_{HF}(1\sigma^2 2\sigma^1 1\pi^1)$=0.9525) which is the only configuration in the MRCISD expansion that has a coefficient larger than 0.15. 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 ($C_{HF}(1\sigma^2 2\sigma^1)$=0.9034). However, in this case, one non-Hartree-Fock configuration has an expansion coefficient larger than 0.15: $C(1\sigma^2 2\sigma^0 3\sigma^2)$=-0.2707. The occupancies of the natural MOs for the ${}^1\Sigma^+$ state are:
$1\sigma^{1.88}2\sigma^{1.74}3\sigma^{0.17}1\pi_x^{0.07}\ 1\pi_y^{0.07}\ 2\pi_x^{0.01}2\pi_y^{0.01}$.

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 $1\sigma^2 2\sigma^2 1\pi^1$, $1\sigma^2 2\sigma^1 1\pi^2$ and $1\sigma^2 1\pi^3$. When the 1π orbital is occupied by three electrons (essentially 2p on C), we obtain a $^2\Pi_i$ state. When two electrons occupy the 1π orbital and the third electron occupies the antibonding 2σ orbital (essentially 2s2p hybrid orbital on C), a $^4\Sigma^-$ state results. Finally, when two electrons occupy the 2σ orbital and one electron occupies the 1π orbital, a $^2\Pi_r$ state results. Among all states with π^1, π^2 and π^3 occupancies, we found the high-spin $^4\Sigma^-$ ($1\sigma^2 1\pi^2 2\sigma^1$) state to be the lowest. The low-spin $^2\Pi_r$ ($1\sigma^2 2\sigma^2 1\pi^1$) and $^2\Pi_i$ ($1\sigma^2 1\pi^3$) states are less stable by 29.4 kcal/mol and 44.8 kcal/mol, respectively (see Table III). We feel confident in predicting that $^4\Sigma^-$ is the ground electronic state of **NaC**. Because

(Table III near here please)

(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: $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2$), $^3\Pi_i$ ($1\sigma^2 2\sigma^1 1\pi^3$) and $^1\Sigma^+$ ($1\sigma^2 1\pi^4$), (Table IV).

(Table IV near here please)

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 $(17s12p5d4f/7s5p3d2f)_{Na}$ + $(14s9p4d3d/7s5p3d2f)_N$ 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 ($^3\Pi_i$) MRCISD 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 each other (Table IV).

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 IV). Both the $^3\Pi_i$ and the $^3\Sigma^-$ states are well represented by Hartree-Fock wave functions ($C_{HF}(1\sigma^2 2\sigma^2 1\pi_x^{\alpha} 1\pi_y^{2})$=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.[10c] 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. Based on 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 V). The $^2\Pi_r$ state was also found to be the ground state when larger

(Table V near here please)

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 $2s^22p^2$ from C), the most likely candidates for low-energy configurations involve $1\sigma^22\sigma^21\pi^2$, $1\sigma^22\sigma^11\pi^3$, $1\sigma^21\pi^4$, or $1\sigma^22\sigma^11\pi^23\sigma^1$ occupancies. We therefore studied the following five low lying electronic states for MgC: $^3\Sigma^-$ ($1\sigma^22\sigma^21\pi^2$), $^3\Pi_i$ ($1\sigma^22\sigma^11\pi^3$), $^1\Sigma^+$ ($1\sigma^21\pi^4$), $^3\Pi_r$ ($1\sigma^22\sigma^21\pi^13\sigma^1$) and $^5\Sigma^-$ ($1\sigma^22\sigma^11\pi^23\sigma^1$), and the results of our calculations appear in Table VI.

(Table VI near here please)

We find the $^3\Sigma^-$ ($1\sigma^22\sigma^21\pi^2$) state to be the ground state and the $^5\Sigma^-$ ($1\sigma^22\sigma^11\pi^23\sigma^1$) 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 $(17s12p5d4f/7s5p3d2f)_{Mg}$ + $(14s9p4d3d/7s5p3d2f)_C$ basis set. The CASSCF expansion included 260 ($^5\Sigma^-$) and 378 ($^3\Sigma^-$) configurations, which represent all possible distribution 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 VI). 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)[30] 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(Mg-C)=2.099 Å, D_e=1.50 eV and $\Delta G_{1/2}$=527 cm^{-1}) agree well with the BLP data (R_e(Mg-C)=2.103 Å, D_e=1.52 eV and $\Delta G_{1/2}$=541 cm^{-1}) however, for the first excited state, our data $^5\Sigma^-$ (R_e(Mg-C)=2.066 Å, D_e= eV, T_e=3975 cm^{-1} and $\Delta G_{1/2}$=570 cm-1) are somewhat different from those of BLP (R_e(Mg-C)=2.109 Å, D_e=0.66 eV, T_e=3545 cm^{-1} and $\Delta G_{1/2}$=515 cm-1). The quite substantial difference in the bond length (0.043 Å) and $\Delta G_{1/2}$ (55 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 $2s^22p^3$ from N), the most likely candidates for low-energy configurations involve $1\sigma^22\sigma^21\pi^23\sigma^1$, $1\sigma^22\sigma^21\pi^3$, $1\sigma^22\sigma^11\pi^33\sigma^1$ and $1\sigma^22\sigma^11\pi^4$ occupancies. We therefore studied the following four low-lying electronic states: $^4\Sigma^-$ ($1\sigma^22\sigma^21\pi^23\sigma^1$), $^2\Pi_i$ ($1\sigma^22\sigma^21\pi^3$), $^4\Pi_i$ ($1\sigma^22\sigma^11\pi^33\sigma^1$) and $^2\Sigma^+$ ($1\sigma^22\sigma^11\pi^4$). The results of our calculations appear in Table VII.

(Table VII near here please)

We found the <u>high-spin</u> $^4\Sigma^-$ ($1\sigma^22\sigma^21\pi^23\sigma^1$) state to be the ground electronic state and the $^2\Pi_i$ ($1\sigma^22\sigma^21\pi^3$) state to be the lowest lying excited state. However, the adiabatic $X^4\Sigma^- \rightarrow {}^2\Pi_i$ 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 $(17s12p5d4f/7s5p3d2f)_{Na}$ + $(14s9p4d3d/7s5p3d2f)_B$ basis set. The CASSCF expansion included 104 ($^4\Sigma^-$) and 196 ($^2\Pi_i$) configurations, which represent all possible distribution of the 7 valence electrons (two electrons occupy the 1σ-MO in all cases) 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 VII. 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 $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^\alpha 1\pi_y^\alpha)=0.3137$ and $C(1\sigma^2 2\sigma^1 3\sigma^2 1\pi_x^\alpha 1\pi_y^\alpha)=0.8770$ for $^4\Sigma^-$ and $C_{HF}(1\sigma^2 2\sigma^2 1\pi_x^\alpha 1\pi_y^2)=0.8327$ for $^3\Pi_i$) in the MRCISD wave function at the optimal bond lengths. At R(Mg-N)=2.100 Å and shorter distances, the dominant configuration in the $^4\Sigma^-$ state is $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^\alpha 1\pi_y^\alpha)=0.9526$ and all other configurations in MRCISD expansion have coefficients less than 0.15 in magnitude. At the equilibrium internuclear distance, the $(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^\alpha 1\pi_y^\alpha)$ configuration has a coefficient of 0.3137 while the $C(1\sigma^2 2\sigma^1 3\sigma^2 1\pi_x^\alpha 1\pi_y^\alpha)=0.8770$ 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 ($C_{HF}(1\sigma^2 2\sigma^2 3\sigma^0 1\pi_x^\alpha 1\pi_y^2)=0.8327$) remains the same along the potential energy curve, but two other configurations $C(1\sigma^2 2\sigma^0 2\sigma^2 1\pi_x^\alpha 1\pi_y^2)=-0.3482$ and $C(1\sigma^2 2\sigma^\alpha 2\sigma^\alpha 1\pi_x^\beta 1\pi_y^2)=-0.2806$ have amplitudes larger than 0.15. The

occupancies of the 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 MgN ($^4\Sigma^-$) is 0.50 eV at the QCISD(T)/6-311+G(2df) level.

AlB. The two valence isoelectronic molecules B_2 and Al_2 are known to have $^3\Sigma_g^-$,[1,31] and $^3\Pi_u$[32] ground electronic states, respectively. However, the B_2 molecule has a very low-lying $^5\Sigma_u^-$ first excited state (T_e=1701 cm^{-1},[31]) and Al_2 has a low-lying $^3\Sigma_g^-$ first excited state (T_e=200 cm^{-1},[32]). Therefore, for AlB 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 VIII).

(Table VIII near here please)

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 AlB. 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 6 valence electrons in 8 valence active MOs (giving 1512 CSFs). The three lowest triplet roots were then calculated using the 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 the CASSCF-MRCISD(Q) level using a $(17s12p5d4f/7s5p3d2f)_{Al}$ + $(14s9p4d3d/7s5p3d2f)_B$ basis set. The CASSCF expansion included 378 ($^3\Sigma^-$) and 384 ($^3\Pi_r$) configurations, which represent all possible distribution of 6 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 1,155,606 ($^3\Sigma^-$) and 1,154,220 ($^3\Pi_r$) MRCISD configurations. Results of these calculations are presented in Table VIII.

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 $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^0 1\pi_x^\alpha 1\pi_y^\alpha)=0.8952$ for $^3\Sigma^-$ and $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^\alpha 1\pi_x^\alpha)=0.9061$) for $^3\Pi_r$ at the optimal bond lengths.

From more than 1,000,000 configurations in MRCISD expansions, only one non-Hartree-Fock configuration has a coefficient ($C(1\sigma^2 2\sigma^0 3\sigma^2 1\pi_x^1 1\pi_y^1)$=-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 **AlB** be (i) the results are the same at the MCSCF and CASSCF-MRCISD(Q)levels of theory and (ii) B_2 has a $^3\Sigma_g^-$ ground electronic state with a 1701 cm^{-1},[31] excitation energy into $^3\Pi_u$ state, (iii) in Al_2, the $^3\Sigma_g^-$ state is located only 200 cm^{-1} above the $^3\Pi_u$ state.[32] Therefore we expect that in AlB the energy difference between these two states should be somewhere inbetween. Our calculated dissociation energy (D_e) of AlB ($^3\Sigma^-$) 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 $^1\Sigma^+$ ($1\sigma^2 2\sigma^2$), $^3\Sigma^-$ ($1\sigma^2 1\pi^2$) and $^3\Pi_r$ ($1\sigma^2 1\pi^1 2\sigma^1$) 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 $(17s12p5d4f/7s5p3d2f)_{Al}$ +

$(14s9p4d3d/7s5p3d2f)_{Li}$ 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: $^2\Pi_r$ $(1\sigma^2 2\sigma^2 1\pi^1)$, $^2\Sigma^+$ $(1\sigma^2 2\sigma^2 3\sigma^1)$, $^4\Pi_r$ $(1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1)$, $^4\Sigma^-$ $(1\sigma^2 2\sigma^1 1\pi^2)$ and $^2\Pi_i$ $(1\sigma^2 1\pi^3)$ 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 X).

(Table X near here please)

Using 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 6 valence electrons in 8 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 ten 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 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[10c] we studied three $^1\Sigma^+$ ($1\sigma^2 2\sigma^2$), $^3\Sigma^-$ ($1\sigma^2 1\pi^2$) and $^3\Pi_r$ ($1\sigma^2 1\pi^1 2\sigma^1$) low-lying states of LiAl (Table XI), and

(Table XI near here please)

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.

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 $(17s12p5d4f/7s5p3d2f)_{Na}$ + $(14s9p4d3d/7s5p3d2f)_B$ basis sets. The CASSCF expansion included 152 ($^1\Sigma^+$) and 160 ($^3\Pi_r$) configurations, which represent all possible distribution 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 XI).

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 ($C_{HF}(1\sigma^2 2\sigma^2)$=0.9163 for $^1\Sigma^+$ and $C_{HF}(1\sigma^2 2\sigma^1 1\pi_x^{\alpha})$=0.9476 for $^3\Pi_r$). Among all configurations in the MRCISD expansions for both these configurations, only one configuration has a coefficient ($C(1\sigma^2 2\sigma^0 3\sigma^2)$=-0.1656 for $^3\Sigma^-$) 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[11b] we studied five $^1\Sigma^+$ ($1\sigma^2 1\pi^4$), $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2$), $^3\Pi_r$ ($1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$), $^3\Pi_i$ ($1\sigma^2 2\sigma^1 1\pi^3$) and $^5\Sigma^-$ ($1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$) 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 $(17s12p5d4f/7s5p3d2f)_{Mg,Si}$ basis sets. The CASSCF expansion included 378 ($^3\Sigma^-$) and 384 ($^3\Pi_r$) configurations, which represent all possible distribution of the valence electron among (3,2,2,1) active orbitals. All single- and double-excitations from these CASSCF configurations were than 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 XII).

The $^3\Sigma^-$ state is predicted to be the most stable at

(Table XII near here please)

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 ($C_{HF}(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1)$=0.9035 for $^3\Pi_r$ and $C_{HF}(1\sigma^2 2\sigma^2 1\pi_x^\alpha 1\pi_y^\alpha)$=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 ($C(1\sigma^2 2\sigma^0 3\sigma^2 1\pi_x^\alpha 1\pi_y^\alpha)$=-0.2459 for $^3\Sigma^-$). The occupancies of the natural MO for the $^1\Sigma^+$ 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[14] we found two electronic states $^4\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$) and $^2\Pi_i$ ($1\sigma^2 2\sigma^2 1\pi^3$) to be the most stable for BeP. At the PMP4/6-311+G(2df) and at QCISD(T)/6-311+G(2df) levels, the $^2\Sigma^+$ state is lower by only 3.1and 3.5 kcal/mol, respectively. Calculations on these two states at the CASSCF-MRCISD(Q) level using a $(17s12p5d4f/7s5p3d2f)_P$ + $(14s9p4d3d/7s5p3d2f)_{Be}$ basis set produced expansions with 104 ($^4\Sigma^-$) and 196 ($^2\Pi_i$) configurations, which represent all possible distributions of 7 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 XIII).

The $^4\Sigma^-$ state is found to be

(Table XIII near here please)

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 ($C_{HF}(1\sigma^2 2\sigma^2 3\sigma^\alpha 1\pi_x^\alpha 1\pi_y^\alpha)=0.9437$ for $^4\Sigma^-$ and $C_{HF}(1\sigma^2 2\sigma^2 1\pi_x^\alpha 1\pi_y^2)=0.9098$ 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.

BP. Previously,[14] 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 $(17s12p5d4f/7s5p3d2f)_P$ + $(14s9p4d3d/7s5p3d2f)_{Be}$ basis sets. The CASSCF expansion included 142 ($^1\Sigma^+$) and 150 ($^3\Pi_i$) configurations, which represent all possible distribution of the 7 valence electrons (two electrons occupy the 1σ-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 1,089,382 ($^1\Sigma^+$) and 1,775,350 ($^3\Pi_i$) 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 XIV) but not identical.

(Table XIV near here please)

The $^3\Pi_i$ state is predicted to be the most stable at both the CASSCF-MRCISD and CASSCF-MRCISD(Q) levels. Because the $^3\Pi_i$ state is the lowest at all sophisticated ab initio levels (PMP4, QCISD(T), CASSCF-MRCISD and CASSCF-MRCISD(Q)) we are reasonably confident that $^3\Pi_i$ is the ground state for **BP**.

Both the $^1\Sigma^+$ and $^3\Pi_i$ states are well represented by Hartree-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 $C_{HF}(1\sigma^2 2\sigma^2 2\sigma^1 1\pi_x^\alpha 1\pi_y^2)$= 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: $1\sigma^{1.96}2\sigma^{1.82}3\sigma^{0.16}4\sigma^{0.02}1\pi_x^{1.86}1\pi_y^{1.86}\,2\pi_x^{0.11}2\pi_y^{0.11}$ and $1\sigma^{1.96}2\sigma^{1.90}3\sigma^{1.00}4\sigma^{0.03}1\pi_x^{0.97}1\pi_y^{1.87}2\pi_x^{0.06}2\pi_y^{0.10}$, respectively.

SiP. In our previous study[14] 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 $(17s12p5d4f/7s5p3d2f)_{Si,P}$ basis sets. The CASSCF expansion included 208 ($^2\Sigma^+$) and 196 ($^2\Pi_i$) configurations, which represent all possible distribution of the 7 valence electrons (two electrons occupy the 1σ-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 XV).

(Table XV near here please)

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 three 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 ($C_{HF}(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2)=0.9042$ for $^2\Sigma^+$ and $C_{HF}(1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^\alpha 1\pi_y^2)=0.9187$ 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:

$1\sigma^{2.00}2\sigma^{1.90}3\sigma^{1.00}4\sigma^{0.03}1\pi_x^{1.87}1\pi_y^{1.87}\,2\pi_x^{0.10}2\pi_y^{0.10}$ and
$1\sigma^{2.00}2\sigma^{1.94}3\sigma^{1.90}4\sigma^{0.97}1\pi_x^{0.97}1\pi_y^{1.87}\,2\pi_x^{0.06}2\pi_y^{0.10}$, 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 XVI the theoretical and available experimental dissociation energies for these ground states are presented.

(Figure 2 and Table XVI near here please)

In Table XVI 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 site all of the theoretical data published in the literature but select what we feel is the most reliable data.

The conventional <u>valence</u> MO ordering for first-row <u>homonuclear</u> 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.[33] 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 Fig. 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 Fig. 2 in green, most first and second 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 ($^2\Sigma^+$ $(1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1)$),

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, twenty diatomics (marked in red in Fig. 2) do not fit the pattern and have unexpected 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 2σ- and 1π-MOs or of the 1π - and 3σ MOs. For example, the $1\sigma^2 2\sigma^2 1\pi^0$

states lie slightly above the corresponding $1\sigma^2 2\sigma^1 1\pi^1$ states for LiB and NaB, and the $1\sigma^2 2\sigma^2 1\pi^1$ states are above the $1\sigma^2 2\sigma^1 1\pi^2$ states for LiC, NaC, LiSi, and NaSi.

Another group of high-spin ground state molecules arise because of quasi-degeneracy between the 1π and 3σ-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, 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, AlP, and Si_2. These two groups of "peculiar" species arise when there are 4-5 or 7-8 valence electrons.

Clearly, the isoelectronic principle[34], 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 Figures 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 ordering arise. Even greater challanges arise when considering three- or larger atomic clusters especially when group 3, 4 or 5 elements are involved.

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Figure Captions

Figure 1. The 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.

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

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.

Table I. Calculated Molecular Properties of the Lowest BeB states.

BeB ($^2\Pi_r$)	BeB ($^2\Sigma^+$)	BeB ($^4\Pi_r$)	BeB ($^4\Sigma^-$)	BeB ($^2\Pi_i$)
$1\sigma^2 2\sigma^2 1\pi^1$	$1\sigma^2 2\sigma^2 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^2$	$1\sigma^2 1\pi^3$
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(Be-B)=1.922 Å	R_e(Be-B)=2.085 Å	R_e(Be-B)=1.828 Å	R_e(Be-B)=1.684 Å	R_e(Be-B)=1.492 Å
ω_e=680 cm^{-1}	ω_e=575 cm^{-1}	ω_e=839 cm^{-1}	ω_e=1102 cm^{-1}	ω_e=1392 cm^{-1}
$<S^2>$=0.759	$<S^2>$=0.772	$<S^2>$=3.755	$<S^2>$=3.836	$<S^2>$=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(Be-B)= 1.962Å	R_e(Be-B)=2.113 Å	R_e(Be-B)=1.833 Å	R_e(Be-B)=1.719 Å	R(Be-B)=1.492 Å
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	EQCISD(T)=-39.22319	
$<S^2>$=0.763	$<S^2>$=0.776	$<S^2>$=3.757	$<S^2>$=3.862	$<S^2>$=0.938
T_{ePMP4}=0.0 kcal/mol	T_{ePMP4}=7.9 kcal/mol	T_{ePMP4}=9.6 kcal/mol	T_{ePMP4}=11.0 kcal/mol	T_{ePMP4}=69.3 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=9.2 kcal/mol	$T_{eQCISD(T)}$=13.0 kcal/mol	$T_{eQCISD(T)}$=13.5 kcal/mol	

Table II. 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(Na-B)=2.490 Å	R_e(Na-B)=2.708 Å	R_e(Na-B)=2.287 Å
ω_e=354 cm^{-1}	ω_e=302 cm^{-1}	ω_e=407 cm^{-1}
$<S^2>$=2.013		$<S^2>$=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(Na-B)=2.520 Å	R_e(Na-B)=2.770 Å	R(Na-B)=2.287 Å
EPMP4=-186.46799	E_{MP4}=-186.45970	E_{MP4}=-186.44770
$E_{QCISD(T)}$=-186.47046	$E_{QCISD(T)}$=-186.46549	$E_{QCISD(T)}$=-186.45230
$<S^2>$=2.016		$<S^2>$=2.059
T_{ePMP4}=0.0 kcal/mol	T_{eMP4}=5.2 kcal/mol	T_{eMP4}=12.7 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=3.1 kcal/mol	$T_{eQCISD(T)}$=11.4 kcal/mol
CASSCF-MRCISD	CASSCF-MRCISD	
R_e(Na-B)=2.526 Å	R_e(Na-B)=2.757 Å	
ω_e=329 cm^{-1}	ω_e=255 cm^{-1}	
$E_{CASSCF\text{-}MRCISD}$=-186.48765	$E_{CASSCF\text{-}MRCISD}$=-186.48361	
$T_{eCASSCF\text{-}MRCISD}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD}$=2.5 kcal/mol	
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)	
R_e(Na-B)=2.526 Å	R_e(Na-B)=2.757 Å	
ω_e=329 cm^{-1}	ω_e=255 cm^{-1}	
$E_{CASSCF\text{-}MRCISD(Q)}$=-186.48847	$E_{CASSCF\text{-}MRCISD(Q)}$=-186.48421	
$T_{eCASSCF\text{-}MRCISD(Q)}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD(Q)}$=2.7 kcal/mol	

Table III. Calculated Molecular Properties of the lowest NaC states.

NaC ($^4\Sigma^-$)	NaC ($^2\Pi_r$)	NaC ($^2\Pi_i$)
$1\sigma^2 1\pi^2 2\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^1$	$1\sigma^2 1\pi^3$
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}=-186.56706
R_e(Na-C)=2.251 Å	R_e(Na-C)=2.505 Å	R_e(Na-C)=2.135 Å
ω_e=443 cm^{-1}	ω_e=401 cm^{-1}	ω_e=474 cm^{-1}
$<S^2>$=3.756	$<S^2>$=0.815	$<S^2>$=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(Na-C)=2.264 Å	R(Na-C)=2.505 Å	R(Na-C)=2.135 Å
EPMP4=-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
$<S^2>$=2.756	$<S^2>$=0.817	$<S^2>$=0.792
T_{ePMP4}=0.0 kcal/mol	T_{eMP4}=32.5 kcal/mol	T_{eMP4}=50.3 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=29.4 kcal/mol	$T_{eQCISD(T)}$=44.8 kcal/mol

Table IV. Calculated Molecular Properties of the lowest NaN states.

NaN ($^3\Sigma^-$)	NaN ($^3\Pi_i$)	NaN ($^1\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^2$	$1\sigma^2 1\pi^3 2\sigma^1$	$1\sigma^2 1\pi^4$
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(Na-N)=2.591 Å	R_e(Na-N)=2.104 Å	R_e(Na-N)=2.011 Å
ω_e=144 cm^{-1}	ω_e=484 cm^{-1}	ω_e=475 cm^{-1}
$<S^2>$=2.895	$<S^2>$=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(Na-N)=2.287 Å	R_e(Na-N)=2.120 Å	R(Na-N)=2.011 Å
E_{PMP4}=-216.36767	EPMP4=-216.37615	E_{MP4}=-216.29664
$E_{QCISD(T)}$=-216.38550	$E_{QCISD(T)}$=-216.37586	$E_{QCISD(T)}$=-216.30965
$<S^2>$=2.837	$<S^2>$=2.058	
T_{eMP4}=5.3 kcal/mol	T_{ePMP4}=0.0 kcal/mol	T_{eMP4}=44.6 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=6.0 kcal/mol	$T_{eQCISD(T)}$=47.6 kcal/mol
CASSCF-MRCISD	CASSCF-MRCISD	
R_e(Na-N)=2.282 Å	R_e(Na-N)=2.117 Å	
ω_e=379 cm^{-1}	ω_e=465 cm^{-1}	
$E_{CASSCF\text{-}MRCISD}$=-216.41352	$E_{CASSCF\text{-}MRCISD}$=-216.40139	
$T_{eCASSCF\text{-}MRCISD}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD}$=7.6 kcal/mol	
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)	
R_e(Na-N)=2.284 Å	R_e(Na-N)=2.121 Å	
ω_e=379 cm^{-1}	ω_e=461 cm^{-1}	
$E_{CASSCF\text{-}MRCISD(Q)}$=-216.41918	$E_{CASSCF\text{-}MRCISD(Q)}$=-216.40621	
$T_{eCASSCF\text{-}MRCISD(Q)}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD(Q)}$=8.1 kcal/mol	

Table V. 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}=-224.35127		E_{MP2}=-224.33561	E_{MP2}=-224.32603	E_{MP2}=-224.20474
R_e(Mg-B)=2.473 Å	No minimum	R_e(Mg-B)=2.263 Å	R_e(Mg-B)=2.117 Å	R_e(Mg-B)=1.983 Å
ω_e=269 cm^{-1}		ω_e=510 cm^{-1}	ω_e=568 cm^{-1}	ω_e=630 cm^{-1}
$<S^2>$=0.768		$<S^2>$=3.757	$<S^2>$=3.881	$<S^2>$=1.671
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(Mg-B)=2.390 Å	R_e(Mg-B)=2.775 Å	R(Mg-B)=2.263 Å	R(Mg-B)=2.117 Å	R(Mg-B)=1.983 Å
E_{MP4}=-224.24634	E_{MP4}=-224.23560	EPMP4=-224.21964	EPMP4=-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	
$<S^2>$=0.768	$<S^2>$=0.859	$<S^2>$=3.759	$<S^2>$=3.821	$<S^2>$=1.672
T_{eMP4}=0.0 kcal/mol	T_{eMP4}=6.7 kcal/mol	T_{ePMP4}=16.8 kcal/mol	T_{ePMP4}=20.2 kcal/mol	T_{eMP4}=88.1 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=9.1 kcal/mol	$T_{eQCISD(T)}$=19.7 kcal/mol	$T_{eQCISD(T)}$=20.1 kcal/mol	

Table VI. Calculated Molecular Properties of the lowest MgC states.

MgC ($^3\Sigma^-$)	MgC ($^5\Sigma^-$)	MgC ($^3\Pi_r$)	MgC ($^3\Pi_i$)	MgC ($^1\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^2$	$1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$	$1\sigma^2 1\pi^3 2\sigma^1$	$1\sigma^2 1\pi^4$
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(Mg-C)=2.087 Å	R_e(Mg-C)=2.064 Å	R_e(Mg-C)=2.280 Å	R_e(Mg-C)=1.966 Å	R_e(Mg-C)=1.834 Å
ω_e=507 cm^{-1}	ω_e=593 cm^{-1}	ω_e= cm^{-1}	ω_e=613 cm^{-1}	ω_e=773 cm^{-1}
$<S^2>$=2.038	$<S^2>$=6.006	$<S^2>$=2.088	$<S^2>$=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(Mg-C)=2.083 Å	R_e(Mg-C)=2.062 Å	R(Mg-C)=2.280 Å	R(Mg-C)=1.966 Å	R(Mg-C)=1.834 Å
E_{MP4}=-237.45647	E_{PMP4}=-237.45479	EPMP4=-237.42256	EPMP4=-237.37813	E_{MP4}=-237.30181
$E_{QCISD(T)}$=-237.47358	$E_{QCISD(T)}$=-237.45680	$E_{QCISD(T)}$=-237.42660	$E_{QCISD(T)}$=-237.39372	
$<S^2>$=2.035	$<S^2>$=6.005	$<S^2>$=2.087	$<S^2>$=2.042	
T_{eMP4}=0.0 kcal/mol	T_{ePMP4}=1.0 kcal/mol	T_{ePMP4}=21.3 kcal/mol	T_{ePMP4}=48.1 kcal/mol	T_{eMP4}=97.0 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=10.5 kcal/mol	$T_{eQCISD(T)}$=29.5 kcal/mol	$T_{eQCISD(T)}$=50.1 kcal/mol	
CASSCF-MRCISD	CASSCF-MRCISD			
R_e(Mg-C)=2.094 Å	R_e(Mg-C)=2.065 Å			
ω_e=543 cm^{-1}	ω_e=573 cm^{-1}			
$E_{CASSCF-MRCISD}$= -237.48796	$E_{CASSCF-MRCISD}$= -237.47211			
$T_{eCASSCF-MRCISD}$=0.0 kcal/mol	TeCASSCF-MRCISD=9.9 kcal/mol			
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)			
R_e(Mg-C)=2.099 Å	R_e(Mg-C)=2.066 Å			
ω_e=536 cm^{-1}	ω_e=572 cm^{-1}			
$E_{CASSCF-MRCISD(Q)}$= -237.49350	$E_{CASSCF-MRCISD(Q)}$= -237.47539			
$T_{eCASSCF-MRCISD(Q)}$= 0.0 kcal/mol	TeCASSCF-MRCISD(Q)= 11.4 kcal/mol			

Table VII. Calculated molecular properties of the lowest MgN states.

MgN ($^4\Sigma^-$)	MgN ($^2\Pi_i$)	MgN ($^4\Pi_i$)	MgN ($^2\Sigma^+$)
$1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^3$	$1\sigma^2 2\sigma^1 1\pi^3 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^4$
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(Mg-N)=2.068 Å	R_e(Mg-N)=1.857 Å	R_e(Mg-N)=1.944 Å	R(Mg-N)=1.847 Å
ω_e=574 cm^{-1}	ω_e=827 cm^{-1}	ω_e=619 cm^{-1}	ω_e=637 cm^{-1}
$<S^2>$=3.806	$<S^2>$=0.766	$<S^2>$=3.766	$<S^2>$=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(Mg-N)=2.084 Å	R_e(Mg-N)=1.929 Å	R(Mg-N)=1.944 Å	R(Mg-N)=1.847 Å
EPMP4=-254.16784	E_{MP4}=-254.150029	E_{MP4}=-254.13459	EPMP4=-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 kcal/mol	T_{ePMP4}=11.2 kcal/mol	T_{eMP4}=20.9 kcal/mol	T_{ePMP4}=66.8 kcal/mol
$Te_{QCISD(T)}$=0.0 kcal/mol	$Te_{QCISD(T)}$=6.3 kcal/mol	$Te_{QCISD(T)}$=21.0 kcal/mol	$Te_{QCISD(T)}$=52.6 kcal/mol
CASSCF-MRCISD	CASSCF-MRCISD		
R_e(Mg-N)=2.038 Å	R_e(Mg-N)=1.925 Å		
ω_e=942 cm^{-1}	ω_e=631 cm^{-1}		
$E_{CASSCF-MRCISD}$=-254.18311	$E_{CASSCF-MRCISD}$=-254.17687		
$Te_{CASSCF-MRCISD}$=0.0 kcal/mol	$Te_{CASSCF-MRCISD}$=3.9 kcal/mol		
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)		
R_e(Mg-N)=2.133 Å	R_e(Mg-N)=1.929 Å		
ω_e=730 cm^{-1}	ω_e=627 cm^{-1}		
$E_{CASSCF-MRCISD(Q)}$= -254.19718	$E_{CASSCF-MRCISD(Q)}$= -254.18630		
$Te_{CASSCF-MRCISD(Q)}$=0.0 kcal/mol	$Te_{CASSCF-MRCISD(Q)}$=6.8 kcal/mol		

Table VIII. Calculated molecular properties of the lowest AlB states.

AlB ($^3\Sigma^-$)	AlB ($^3\Pi_r$)	AlB ($^5\Sigma^-$)
$1\sigma^2 2\sigma^2 1\pi^2$	$1\sigma^2 2\sigma^2 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^2 3\sigma^1$
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(Al-B)=2.019 Å	R_e(Al-B)=2.212 Å	R_e(Al-B)=1.943 Å
ω_e=651 cm^{-1}	ω_e=521 cm^{-1}	ω_e=792 cm^{-1}
$<S^2>$=2.644	$<S^2>$=2.014	$<S^2>$=6.002
MCSCF//MCSCF	MCSCF//MCSCF	
R_e(Al-B)=2.088 Å	R_e(Al-B)=2.261 Å	
ω_e=574 cm^{-1}	ω_e=471 cm^{-1}	
E_{MCSCF}=-266.50779	E_{MCSCF}=-266.50371	
Te_{MCSCF}=0.0 kcal/mol	Te_{MCSCF}=2.6 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(Al-B)=2.056 Å	R_e(Al-B)=2.226 Å	R(Al-B)=1.943 Å
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 kcal/mol	T_{ePMP4}=0.0 kcal/mol	T_{ePMP4}=17.4 kcal/mol
$T_{eQCISD(T)}$=0.2 kcal/mol	$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=22.6 kcal/mol
CASSCF-MRCISD	CASSCF-MRCISD	
R_e(Al-B)=2.046 Å	R_e(Al-B)=2.224 Å	
ω_e=608 cm^{-1}	ω_e=493 cm^{-1}	
$E_{CASSCF\text{-}MRCISD}$=-266.60194	$E_{CASSCF\text{-}MRCISD}$=-266.59809	
$T_{eCASSCF\text{-}MRCISD}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD}$=2.4 kcal/mol	
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)	
R_e(Al-B)=2.051 Å	R_e(Al-B)=2.237 Å	
ω_e=600 cm^{-1}	ω_e=482 cm^{-1}	
$E_{CASSCF\text{-}MRCISD(Q)}$=-266.60845	$E_{CASSCF\text{-}MRCISD(Q)}$=-266.60585	
$T_{eCASSCF\text{-}MRCISD(Q)}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD(Q)}$=1.6 kcal/mol	

Table IX. 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(Na-Al)=3.134 Å	R_e(Na-Al)=2.985 Å	R_e(Na-Al)=2.673 Å
ω_e=196 cm^{-1}	ω_e=184 cm^{-1}	ω_e=259cm^{-1}
	$<S^2>$=2.024	$<S^2>$=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(Na-Al)=3.182 Å	R_e(Na-Al)=3.007 Å	R_e(Na-Al)=2.739 Å
E_{MP4}=-403.79651	EPMP4=-403.79027	E_{PMP4}=-403.76274
$E_{QCISD(T)}$=-403.80002	$E_{QCISD(T)}$=-403.79176	$E_{QCISD(T)}$=-403.76424
	$<S^2>$=2.027	$<S^2>$=2.018
T_{eMP4}=0.0 kcal/mol	T_{ePMP4}=3.9 kcal/mol	TePMP4=21.2 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=5.2 kcal/mol	$T_{eQCISD(T)}$=22.4 kcal/mol

Table X. Calculated Molecular Properties of the Lowest MgAl states.

MgAl ($^2\Pi_r$)	MgAl ($^2\Sigma^+$)	MgAl ($^4\Pi_r$)	MgAl ($^4\Sigma^-$)	MgAl ($^2\Pi_i$)
$1\sigma^2 2\sigma^2 1\pi^1$	$1\sigma^2 2\sigma^2 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^1 3\sigma^1$	$1\sigma^2 2\sigma^1 1\pi^2$	$1\sigma^2 2\sigma^0 1\pi^3$
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}=-441.79210	E_{MP2}=-441.78656	E_{MP2}=-441.75046	E_{MP2}=-441.74582	E_{MP2}=-441.61817
R_e(Mg-Al)=2.922 Å	R_e(Mg-Al)=3.327 Å	R_e(Mg-Al)=2.723 Å	R_e(Mg-Al)=2.484 Å	R_e(Mg-Al)=2.355 Å
ω_e=192 cm^{-1}	ω_e=95 cm^{-1}	ω_e=297 cm^{-1}	ω_e=213 cm^{-1}	ω_e=361 cm^{-1}
$<S^2>$=0.781	$<S^2>$=0.848	$<S^2>$=3.758	$<S^2>$=3.859	$<S^2>$=1.732
MCSCF//MSSCF	MCSCF//MSSCF			
R(Mg-Al)=3.03 Å	R(Mg-Al)=3.22 Å			
ω_e=131 cm^{-1}	ω_e=178 cm^{-1}			
E_{MCSCF}=-441.53167	E_{MCSCF}=-441.50779			
Te=0.0 kcal/mol	Te=15.0 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(Mg-Al)=2.901 Å	R_e(Mg-Al)=3.269 Å	R_e(Mg-Al)=2.750 Å	R_e(Mg-Al)=2.536 Å	R(Mg-Al)=2.355 Å
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	EQCISD(T)=-441.57131	EQCISD(T)=-441.52980	EQCISD(T)=-441.53089	$E_{QCISD(T)}$=-441.42436
T_{ePMP4}=0.0 kcal/mol	T_{ePMP4}=3.7 kcal/mol	T_{ePMP4}=29.7 kcal/mol	T_{ePMP4}=30.9 kcal/mol	T_{ePMP4}=103.6 kcal/mol
$T_{eQCISD(T)}$=0.0 kcal/mol	$T_{eQCISD(T)}$=4.5 kcal/mol	$T_{eQCISD(T)}$=30.5 kcal/mol	$T_{eQCISD(T)}$=29.8 kcal/mol	$T_{eQCISD(T)}$=96.7 kcal/mol

Table XI. Calculated molecular properties of the lowest LiAl states.

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

Table XII. Calculated molecular properties of the lowest MgSi states.

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

Table XIII. Calculated molecular properties of the lowest BeP states.

BeP ($^4\Sigma^-$)	BeP($^2\Pi_r$)
$1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$	$1\sigma^2 2\sigma^2 1\pi^3$
CASSCF-MRCISD	CASSCF-MRCISD
R_e(Be-P)=2.063 Å	R_e(Be-P)=1.924 Å
ω_e=627 cm^{-1}	ω_e=778 cm^{-1}
$E_{CASSCF\text{-}MRCISD}$=-355.47841	$E_{CASSCF\text{-}MRCISD}$=-355.47367
$T_{eCASSCF\text{-}MRCISD}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD}$=3.0 kcal/mol
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)
R_e(Be-P)=2.082 Å	R_e(Be-P)=1.927 Å
ω_e=586 cm^{-1}	ω_e=770 cm^{-1}
$E_{CASSCF\text{-}MRCISD(Q)}$=-355.49071	$E_{CASSCF\text{-}MRCISD(Q)}$=-355.48606
$T_{eCASSCF\text{-}MRCISD(Q)}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD(Q)}$=2.9 kcal/mol

Table XIV. 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(B-P)=1.755 Å	R_e(B-P)=1.684 Å
ω_e=920 cm^{-1}	ω_e=1038 cm^{-1}
$E_{CASSCF\text{-}MRCISD}$=-365.53221	$E_{CASSCF\text{-}MRCISD}$=-365.52083
$T_{eCASSCF\text{-}MRCISD}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD}$=7.1 kcal/mol
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)
R_e(B-P)=1.765 Å	R_e(B-P)=1.687 Å
ω_e=897 cm^{-1}	ω_e=1026 cm^{-1}
$E_{CASSCF\text{-}MRCISD(Q)}$=-365.55024	$E_{CASSCF\text{-}MRCISD(Q)}$=-365.53602
$T_{eCASSCF\text{-}MRCISD(Q)}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD(Q)}$=8.9 kcal/mol

Table XV. 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(Si-P)=2.092 Å	R_e(Si-P)=2.011 Å
ω_e=608 cm^{-1}	ω_e=638 cm^{-1}
$E_{CASSCF\text{-}MRCISD}$=-629.79935	$E_{CASSCF\text{-}MRCISD}$=-629.79603
$T_{eCASSCF\text{-}MRCISD}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD}$=2.1 kcal/mol
CASSCF-MRCISD(Q)	CASSCF-MRCISD(Q)
R_e(Si-P)=2.092 Å	R_e(Si-P)=2.012 Å
ω_e=608 cm^{-1}	ω_e=629 cm^{-1}
$E_{CASSCF\text{-}MRCISD(Q)}$=-629.80846	$E_{CASSCF\text{-}MRCISD(Q)}$=-629.80502
$T_{eCASSCF\text{-}MRCISD(Q)}$=0.0 kcal/mol	$T_{eCASSCF\text{-}MRCISD(Q)}$=2.2 kcal/mol

Table XVI. Calculated and experimental ground state dissociation energies (D) of diatomic molecules contains first and second row atoms

Molecule	D (eV) calculated	D (eV), experimental
H_2, $^1\Sigma_g^+$	4.478071[a]	4.478077[b]
HLi, $^1\Sigma^+$	2.415[c]	2.429[d]
HBe, $^2\Sigma^+$	2.047[c]	2.034[d]
HB, $^1\Sigma^+$	3.647[e]	3.42[b]
HC, $^2\Pi_r$	3.443[c], 3.577[e]	3.465[d]
HN, $^3\Sigma^-$	3.339[c], 3.499[e]	<3.47[d]
HO, $^2\Pi^i$	4.380[c], 4.518[e]	4.392[d]
HF, $^1\Sigma^+$	5.915[c] , 5.984[e]	5.869[d]
HMg, $^2\Sigma^+$	1.27[f]	1.34[d]
HAl, $^1\Sigma^+$	3.174[g]	<3.06[d] , 3.170[g]
HSi, $^2\Pi_r$	3.161[g]	3.06[d] , 3.161[g]
HP, $^3\Sigma^-$	3.135[g]	3.122[g]
HS, $^2\Pi_i$	3.721[g]	3.55[d] , 3.764[g]
HCl, $^1\Sigma^+$	4.653[g]	4.434[d] , 4.653[g]
Li_2, $^1\Sigma_g^+$	1.02, 1.140[c]	1.046[d]
LiBe, $^2\Sigma^+$	0.26[h], 0.29[i], 0.25[j]	
LiB, $^3\Pi$	1.18[h] , 1.11[k]	
LiC, $^4\Sigma^-$	2.58[h]	
LiN, $^3\Sigma^-$	1.49[h], 1.61[f]	
LiO, $^2\Pi^i$	3.48[h] , 3.78[l], 3.30[f]	3.49[d]
LiF, $^1\Sigma^+$	5.81[h], 5.980[c] , 6.06[l]	5.91[d]
LiNa, $^1\Sigma^+$	0.85[h],	0.90[d]
LiMg, $^2\Sigma^+$	0.18[h], 0.20[i]	
LiAl, $^1\Sigma^+$	1.01[h],	
LiSi, $^4\Sigma^-$	1.83[h],	1.54[m]
LiP, $^3\Sigma^-$	1.66[h]	2.53[n]
LiS, $^2\Pi_i$	3.08[h], 3.30[l]	
LiCl, $^1\Sigma^+$	4.76[h], 4.89[l], 4.86[f]	4.84[d]
Be_2, $^1\Sigma_g^+$	0.09[i], 0.08-0.10[o]	0.10[p]
BeB, $^2\Pi$	1.57[q]	
BeC, $^3\Sigma^-$	2.39[r]	
BeN, $^4\Sigma^-$	1.34[s]	
BeO, $^1\Sigma^+$	4.69[l]	4.60[d]
BeF, $^2\Sigma^+$	5.94[l], 5.71[f]	5.85[d], 6.26
BeNa, $^2\Sigma^+$	0.14[i]	
BeMg, $^1\Sigma^+$	0.008[t]	
BeAl, $^2\Pi$	0.40[i]	
BeSi, $^3\Sigma^-$	1.28[u]	
BeP, $^4\Sigma^-$	1.06[v]	
BeS, $^1\Sigma^+$	2.29[l], 3.23[f]	3.8[d]

BeCl, $^2\Sigma^+$	3.87[l], 3.84[f]	3.99[d]
B_2, $^3\Sigma_g^-$	2.84[w]	3.02[d]
BC, $^4\Sigma^-$	4.21[x]	4.60[d]
BN, $^3\Pi$	4.56[y]	3.99[z]
BO, $^2\Sigma^+$	8.43[A], 8.32[f]	8.28[d]
BF, $^1\Sigma^+$	7.74[B]	7.81[d]
BNa, $^3\Pi$	0.76[q]	
BMg,	0.47[q]	
BAl, $^3\Sigma^-$	1.78[q]	
BSi, $^4\Sigma^-$	3.15[u]	2.95[d]
BP, $^3\Pi$	3.13[v]	3.56[C]
BS, $^2\Sigma^+$	5.71[f]	6.01[d]
BCl, $^1\Sigma^+$	5.33f, 5.49[D]	5.5[d]
C_2, $^1\Sigma_g^+$	6.26[w], 6.40[f]	6.21[d]
CN, $^2\Sigma^+$	7.623[c] ,	7.76[d]
CO, $^1\Sigma^+$	11.231[c]	11.092[d]
CF, $^2\Pi_r$	5.71[f]	5.67[d]
CNa, $^4\Sigma^-$	1.97[q]	
CMg,	1.50[q]	
CAl, $^4\Sigma^-$	3.3[E]	
CSi, $^3\Pi_i$	4.4[F], 4.29[f]	4.64[d]
CP, $^2\Sigma^+$	4.71[G], 5.33[f]	5.28[d]
CS, $^1\Sigma^+$	7.476[c]	7.355[d]
CCl, $^2\Pi_r$	4.16[f]	3.34[d]
N_2, $^1\Sigma_g^+$	9.10[w], 9.83[x] , 9.70[f]	9.90[d]
NO, $^2\Pi_i$	6.565[c]	
NF, $^3\Sigma^-$	3.30[f,H]	3.5[d]
NNa,	0.77[q]	
NMg,	0.5[q]	
NAl, $^3\Pi$	2.35[l]	
NSi, $^2\Sigma^+$	3.84[G],	
NP, $^1\Sigma^+$	5.35[G],	6.36[d]
NS, $^2\Pi$	4.69[f]	
NCl, $^3\Sigma^-$	2.52[J]	4.8[d]
O_2, $^3\Sigma_g^-$	5.026[c] , 5.08[w],	5.23[d]
OF, $^2\Pi$	2.10[K]	2.23[d]
ONa, $^2\Pi$	2.83[l]	2.60[d]
OMg, $^1\Sigma^+$	2.75[l]	
OAl, $^2\Sigma^+$	4.12[L]	5.27[d]
OSi, $^1\Sigma^+$	8.308[c]	
OP, $^2\Pi_r$	6.01[M]	6.15[d]
OS, $^3\Sigma^-$	5.269[c], 5.29[J]	5.359[d]
OCl, $^2\Pi$	2.689[c]	2.751[d]

F_2, $^1\Sigma_g^+$	1.613[c], 1.518[w]	1.602[d]
FNa, $^1\Sigma^+$	5.00[l], 4.97[f]	5.33[d]
FMg, $^2\Sigma^+$	4.66[l], 4.56[f]	4.75[d]
FAl, $^1\Sigma^+$	6.89[N], 7.01[f]	6.89[d]
FSi, $^2\Pi_r$	6.01[f]	5.57[d]
FP, $^3\Sigma^-$	4.47[J], 4.56[f]	
FS, $^2\Pi$	3.55[f]	<3.3[d]
FCl, $^1\Sigma^+$	2.680[c]	2.617[d]
Na_2, $^1\Sigma_g^+$	0.850[c]	0.720[d]
NaMg, $^2\Sigma^+$	0.11[i]	
NaAl,	0.77[q]	
NaSi, $^4\Sigma^-$	1.46[u]	
NaP, $^3\Sigma^-$	1.21[v]	
NaS, $^2\Pi$	2.66[l]	
NaCl, $^1\Sigma^+$	4.22[l], 4.28[f]	4.23[d]
Mg_2, $^1\Sigma_g^+$	0.0575[o]	0.050[d]
MgAl,	0.34[q]	
MgSi, $^3\Sigma^-$	0.96[u]	
MgP, $^4\Sigma^-$	0.54[v]	
MgS, $^1\Sigma^+$	1.70[l], 2.23[f]	<2.4[d]
MgCl, $^2\Sigma^+$	3.26i, 3.27[f]	3.29[d]
Al_2, $^3\Pi_u$	1.386[P]	1.55[d]
AlSi, $^4\Sigma^-$	2.45[u]	2.34[d]
AlP, $^3\Sigma^-$	2.07[v]	2.20[d]
AlS, $^2\Sigma^+$	3.99[R]	3.84[d]
AlCl, $^1\Sigma^+$	5.25[N], 5.24[f]	5.12[d]
Si_2, $^3\Sigma_g^-$	3.213[c]	3.21[d]
SiP,	3.35v, 3.15[G]	3.73[d]
SiS, $^1\Sigma^+$	6.29[f]	6.42[d]
SiCl, $^2\Pi_r$	4.32[f]	
P_2, $^1\Sigma_g^+$	4.987[c]	
PS, $^2\Pi$	4.29[f]	4.54[d]
PCl, $^3\Sigma^-$	3.19[f]	
S_2, $^3\Sigma_g^-$	4.306[c]	
SCl, $^2\Pi$	2.78[f]	
Cl_2, $^1\Sigma_g^+$	2.511[c]	2.480[d]

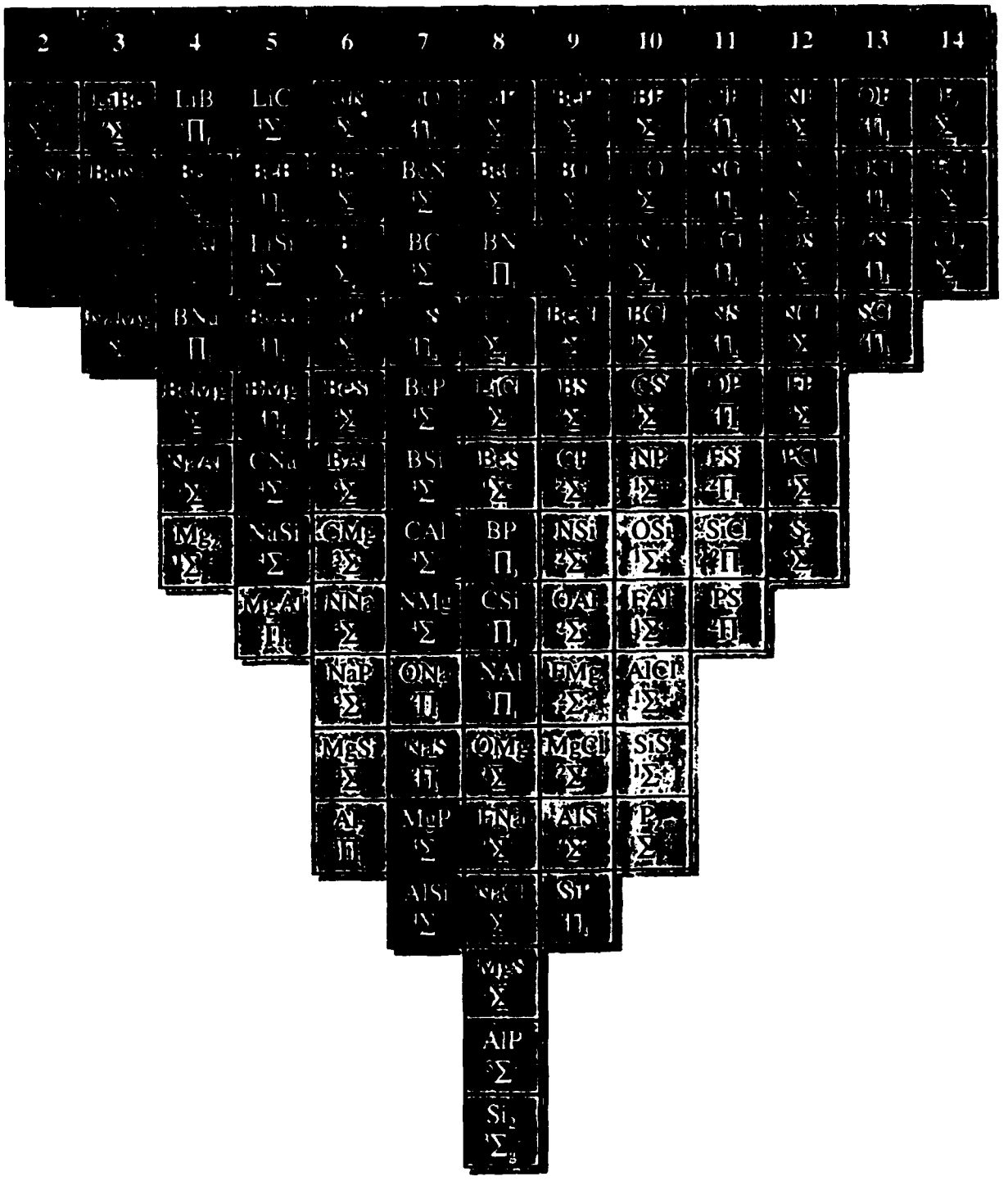
[a] Ref. 35, [b] Ref. 36, [c] Ref. 37, [d] Ref. 1, [e] Ref. 38, [f] Ref. 39, [g] Ref. 40, [h] Ref. 10c, [i] Ref. 13, [j] Ref. 41, [k] Ref. 10b, [l] Ref. 42, [m] Ref. 43, [n] Ref. 44, [o] Ref. 45, [p] Ref. 46, [q] this work, [r] Ref. 17, [s] Ref. 16, [t] Ref. 47, [u] Ref. 11b, [v] Ref. 14, [w] Ref. 48,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

	H	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl
H	H_2 $^1\Sigma_g^+$														
Li	LiH $^1\Sigma^+$	Li_2 $^1\Sigma_g^+$													
Be	BeH $^2\Sigma^+$	BeLi $^2\Sigma^+$	Be_2 $^1\Sigma_g^+$												
B	BH $^1\Sigma^+$	BLi	BBe	B_2 $^3\Sigma_g^-$											
C	CH $^2\Pi_r$	CLi	CBe	CB $^4\Sigma^-$	C_2 $^1\Sigma_g^+$										
N	NH $^3\Sigma^-$	NLi	NBe	NB $^3\Pi_r$	NC $^2\Sigma^+$	N_2 $^1\Sigma_g^+$									
O	OH $^2\Pi_r$	OLi $^2\Pi_r$	OBe $^1\Sigma^+$	OB $^2\Sigma^+$	OC $^1\Sigma^+$	ON $^2\Pi_r$	O_2 $^3\Sigma_g^-$								
F	FH $^1\Sigma^+$	FLi $^1\Sigma^+$	FBe $^2\Sigma^+$	FB $^1\Sigma^+$	FC $^2\Pi_r$	FN $^3\Sigma^-$	FO $^2\Pi_r$	F_2 $^1\Sigma_g^+$							
Na	NaH $^1\Sigma^+$	NaLi $^1\Sigma^+$	NaBe	NaB	NaC	NaN	NaO $^2\Pi_r$	NaF $^1\Sigma^+$	Na_2 $^1\Sigma_g^+$						
Mg	MgH $^2\Sigma^+$	MgLi	MgBe $^1\Sigma^+$	MgB	MgC	MgN	MgO $^1\Sigma^+$	MgF $^2\Sigma^+$	MgNa	Mg_2 $^1\Sigma_g^+$					
Al	AlH $^1\Sigma^+$	AlLi	AlBe	AlB	AlC $^4\Sigma^-$	AlN $^3\Pi_r$	AlO $^2\Sigma^+$	AlF $^1\Sigma^+$	AlNa	AlMg	Al_2 $^3\Pi_u$				
Si	SiH $^2\Pi_r$	SiLi	SiBe	SiB $^4\Sigma^-$	SiC $^3\Pi_r$	SiN $^2\Sigma^+$	SiO $^1\Sigma^+$	SiF $^2\Pi_r$	SiNa	SiMg	SiAl $^4\Sigma^-$	Si_2 $^3\Sigma_g^-$			
P	PH $^3\Sigma^-$	PLi	PBe	PB	PC $^2\Sigma^+$	PN $^1\Sigma^+$	PO $^2\Pi_r$	PF $^3\Sigma^-$	PNa	PMg	PAl	PSi	P_2 $^1\Sigma_g^+$		
S	SH $^2\Pi_r$	SLi	SBe $^1\Sigma^+$	SB $^2\Sigma^+$	SC $^1\Sigma^+$	SN $^2\Pi_r$	SO $^3\Sigma^-$	SF $^2\Pi_r$	SNa	SMg $^1\Sigma^+$	SAl $^2\Sigma^+$	SSi $^1\Sigma^+$	SP $^2\Pi_r$	S_2 $^3\Sigma_g^-$	
Cl	ClH $^1\Sigma^+$	ClLi $^1\Sigma^+$	ClBe $^2\Sigma^+$	ClB $^1\Sigma^+$	ClC $^2\Pi_r$	ClN $^3\Sigma^-$	ClO $^2\Pi_r$	ClF $^1\Sigma^+$	ClNa $^1\Sigma^+$	ClMg $^2\Sigma^+$	ClAl $^1\Sigma^+$	ClSi $^2\Pi_r$	ClP $^3\Sigma^-$	ClS $^2\Pi_r$	Cl_2 $^1\Sigma_g^+$

Figure 1.

	H	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl
H	H_2 $^1\Sigma_g^+$														
Li	LiH $^1\Sigma^+$	Li_2 $^1\Sigma_g^+$													
Be	BeH $^2\Sigma^+$	BeLi $^2\Sigma$	Be_2 $^1\Sigma$												
B	BH $^1\Sigma^+$	BLi $^3\Pi_r$	BBe $^2\Pi_r$	B_2 $^3\Sigma_g^-$											
C	CH $^2\Pi_r$	CLi $^4\Sigma^-$	CBe $^3\Sigma^-$	CB $^4\Sigma^-$	C_2 $^1\Sigma_g^+$										
N	NH $^3\Sigma^-$	NLi $^3\Sigma^-$	NBe $^4\Sigma^-$	NB $^3\Pi_r$	NC $^2\Sigma^+$	N_2 $^1\Sigma_g^+$									
O	OH $^2\Pi_i$	OLi $^2\Pi_i$	OBe $^1\Sigma^+$	OB $^2\Sigma^+$	OC $^1\Sigma^+$	ON $^2\Pi_r$	O_2 $^3\Sigma_g^-$								
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_2 $^1\Sigma_g^+$							
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_2 $^1\Sigma_g^+$						
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_2 $^1\Sigma_g^+$					
Al	AlH $^1\Sigma^+$	AlLi $^1\Sigma^+$	AlBe $^2\Pi_r$	AlB $^2\Sigma$	AlC $^4\Sigma^-$	AlN $^3\Pi_r$	AlO $^2\Sigma^+$	AlF $^1\Sigma^+$	AlNa $^1\Sigma^+$	AlMg $^2\Pi_r$	Al_2 $^3\Pi_u$				
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_2 $^3\Sigma_g^-$			
P	PH $^2\Sigma^+$	PLi $^4\Sigma^-$	PBe $^4\Sigma^-$	PB $^3\Pi_i$	PC $^2\Sigma^+$	PN $^1\Sigma^+$	PO $^2\Pi_r$	PF $^3\Sigma^-$	PNa $^3\Sigma$	PMg $^4\Sigma^-$	PAl $^3\Sigma^-$	PSi $^2\Pi_i$	P_2 $^1\Sigma_g^+$		
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 $^1\Sigma^+$	SAl $^2\Sigma^+$	SSi $^1\Sigma^+$	SP $^2\Pi_r$	S_2 $^3\Sigma_g^-$	
Cl	ClH $^1\Sigma^+$	ClLi $^1\Sigma^+$	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 $^2\Pi_r$	ClP $^3\Sigma^-$	ClS $^2\Pi_i$	Cl_2 $^1\Sigma_g^+$

Figure 2.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LiB
LiC
BeN
BN
BC
BNa
BeP
BS
BSi
BP
NaSi
CMg
CAl
NSi
OSi
SiCl
NMg
CSi
OAl
FAl
PS
NaP
ONa
NAl
OMg
AlCl
MgSi
MgCl
SiS
MgP
AlS
AlSi
SiP
MgS
AlP
Si2

Figure 3.