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Zhengting Gan, Daniel J. Grant, Robert J. Harrison, and David A. Dixon

Citation: *The Journal of Chemical Physics* **125**, 124311 (2006); doi: 10.1063/1.2335446

View online: <http://dx.doi.org/10.1063/1.2335446>

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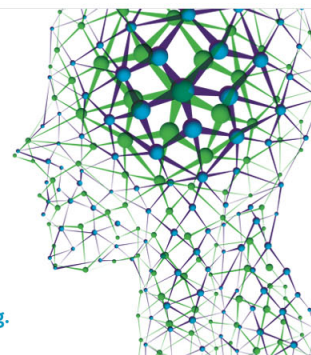
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The lowest energy states of the group-III A–group-V A heteronuclear diatomics: BN, BP, AlN, and AlP from full configuration interaction calculations

Zhengting Gan

Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Daniel J. Grant

Chemistry Department, The University of Alabama, Shelby Hall, Tuscaloosa, Alabama 35487-0336

Robert J. Harrison

Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

David A. Dixon^{a)}

Chemistry Department, The University of Alabama, Shelby Hall, Tuscaloosa, Alabama 35487-0336

(Received 8 June 2006; accepted 13 July 2006; published online 28 September 2006)

Full configuration interaction (CI) calculations on the group-III A–group-V A diatomic molecules BN, BP, AlN, and AlP have been performed with the cc-pVTZ correlation-consistent basis set and compared to CCSD(T) calculations with the same basis set. The CCSD(T) calculations are good to better than 1 kcal/mol in comparison with the full CI results if the T_1 diagnostic is small and to within about 2 kcal/mol if the T_1 diagnostic is large. Inspection of the T_2 amplitudes shows that the simple T_1 diagnostic is providing useful insight into the quality of the starting wave function. The ground state of BN, BP, and AlN is predicted to be the $^3\Pi$ and, for AlP, the ground state is predicted to be $^3\Sigma^-$. For all molecules except BP, there is an excited state within 1.1 kcal/mol of the ground state. The ordering of the state energies can be explained in terms of simple orbital and bonding models. The results provide little evidence for placing the π orbital below the σ orbital for the ground state of these heteronuclear diatomic molecules. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335446]

INTRODUCTION

We are interested in the behavior of group-III A–group-V A compounds for use in chemical hydrogen storage systems. As part of this effort, we have studied the diatomic molecules BN, BP, AlN, and AlP.^{1,2} In our previous studies, we used the CCSD(T) method^{3–5} to treat the correlation of the valence electrons of these molecules in conjunction with the correlation-consistent basis sets.^{6,7} These diatomic molecules are interesting because the molecular orbital occupancies allow for a number of low lying states. This arises because of the possibility of the valence π orbital (based on the valence p orbitals) lying below the σ orbital (based on the valence p orbitals). If the π orbital lies lower than the σ , the molecule forms a $^1\Sigma^+$ state based on the electron configuration $\pi^4\sigma^0$. If the σ orbital is below the π orbital, one obtains the configurations $\sigma^2\pi^2$ and $\sigma^1\pi^3$ which give rise to lowest configurations $^3\Sigma^-$ and $^3\Pi$. Because of the presence of substantial multireference character in some of the states as noted by a large T_1 diagnostic,⁸ it is of interest to see how well the CCSD(T) method is performing for energy differences between these states. In the absence of high-quality experimental results to serve as a benchmark, an optimal way to do this is to use recently developed full configuration interaction (CI) approaches⁹ to calculate the state energy dif-

ferences. The results of our previous CCSD(T) calculations^{1,2} are given in Table I for the state energy differences. The dissociation energies extrapolated to the complete basis set level together with new values for BN ($^3\Sigma^-$) obtained in this study following our previous approach are also given in Table I.

The BN molecule has previously been studied in detail by Martin *et al.*¹⁰ and by Peterson.¹¹ In both publications using multireference calculations, they showed that the ground state is the $^3\Pi$. The prediction of the ground state of

TABLE I. CCSD(T)/CBS state energy differences and D_0 in kcal/mol. Energies are from Refs. 1 and 2 except for BN($^1\Sigma^+$) which is from this work.

| Molecule | CBS | ΔE (0 K) | D_0 (electronic) CBS | D_0 (0 K) |
|----------------------|-------|------------------|------------------------|-------------|
| BN($^3\Pi$) | 0.67 | 0.41 | 104.03 | 102.36 |
| BN($^3\Sigma^-$) | 29.96 | 29.33 | 74.74 | 73.44 |
| BN($^1\Sigma^+$) | 0 | 0 | 104.70 | 102.77 |
| BP($^3\Pi$) | 0 | 0 | 77.19 | 76.45 |
| BP($^3\Sigma^-$) | 20.95 | 20.86 | 56.24 | 55.59 |
| BP($^1\Sigma^+$) | 7.36 | 7.44 | 69.83 | 69.01 |
| AlN($^3\Pi$) | 0.28 | 0.18 | 58.23 | 57.09 |
| AlN($^3\Sigma^-$) | 0 | 0 | 58.51 | 57.27 |
| AlN($^1\Sigma^+$) | 8.57 | 9.45 | 49.94 | 47.82 |
| AlP($^3\Pi$) | 0.09 | 0.18 | 51.63 | 50.74 |
| AlP($^3\Sigma^-$) | 0 | 0 | 51.72 | 50.92 |
| AlPN($^1\Sigma^+$) | 11.19 | 11.67 | 40.53 | 39.25 |

^{a)}Electronic mail: dadixon@bama.ua.edu

BN is complicated by the presence of large multireference character in the $^1\Sigma^+$ state as found by Martin *et al.*¹⁰ and subsequently by Peterson.¹¹ At the CCSD(T)/CBS (CBS is the complete basis set limit obtained by extrapolation) level, the $^1\Sigma^+$ state is lower than the $^3\Pi$ state by 0.7 kcal/mol, similar to the result of Martin *et al.*¹⁰ who calculated the $^1\Sigma^+$ state to be lower than the $^3\Pi$ state by 0.5 kcal/mol at the CCSD(T) level with a [4321] contracted basis set. Using the multireference averaged coupled pair functional approach¹² with the same [4321] basis set, Martin *et al.* found the $^3\Pi$ state to be lower than the $^1\Sigma^+$ state with $T_e=1.32$ kcal/mol (461 cm^{-1}) and provided a best estimate of $T_e=1.1$ kcal/mol (381 cm^{-1}). They calculated a D_e for the $^3\Pi$ ground state of 105.2 kcal/mol based on the dissociation energy of the $^1\Sigma^+$ state and their value of T_e .¹⁰ A later MRCI/CBS calculation by Peterson¹¹ gave $T_e=190\pm 100$ cm^{-1} (0.54 kcal/mol) with a $^3\Pi$ ground state and a bond dissociation energy at the MRCI/CBS limit of 104.2 kcal/mol. Bauschlicher and Partridge¹³ later used essentially the same MRCI approach as that of Peterson and found essentially the same value, 180 ± 110 cm^{-1} . Using the technique of photoelectron spectroscopy on the BN^- ion, T_e has been measured as 0.031 ± 0.004 eV (0.71 kcal/mol).¹⁴ Somewhat earlier, Lorenz *et al.*¹⁵ reported Fourier-transform absorption and laser induced fluorescence spectra of BN in a neon matrix and found a $^3\Pi$ ground state with the $^1\Sigma^+$ state 15–182 cm^{-1} above the ground state. In addition, they find the $^3\Sigma^-$ state with a T_e of 10 332.3 cm^{-1} (29.52 kcal/mol) above the ground state. Ram and Bernath¹⁶ used Fourier-transform infrared emission spectroscopy to observe the $b^3\Pi-a^1\Sigma^+$ transition in the gas phase. We studied¹ these state energies at the R/UCCSD(T)/CBS level and found the $^1\Sigma^+$ state to be below $^3\Pi$ by 0.67 kcal/mol at the R/UCCSD(T)/CBS level for the valence electrons and by 0.41 kcal/mol when all corrections are included. Thus, the CCSD(T) method overestimates the stability of the singlet state. This result is consistent with the study of Denis on the states of BN.¹⁷ He found using the cc-pV5Z basis set that the difference in the CCSD(T) and CCSDT enthalpies of formation of BN in the $^1\Sigma^+$ state is 2.7 kcal/mol and only 0.4 kcal/mol for the $^3\Pi$ state. At the CCSDT/cc-pV5Z level, Denis predicts the $^1\Sigma^+$ state to be above the $^3\Pi$ state by 3.01 kcal/mol. He predicts the $^1\Sigma^+-^3\Pi$ gap to be 0.52 kcal/mol at 298 K at the CCSDTQ level.

Langhoff *et al.*¹⁸ calculated a number of states for AIN at the CASSCF and MRCI levels and suggested that the ground state is $^3\Pi$ with the $^3\Sigma^-$ slightly higher in energy. We found² that the $^3\Sigma^-$ is slightly below the $^3\Pi$ at the R/UCCSD(T) level but the energies of the two states are very close with an electronic energy difference of 0.28 kcal/mol and an energy difference of only 0.19 kcal/mol when other corrections are included. In contrast to BN, the $^1\Sigma^+$ state is 8.57 kcal/mol higher in energy at the valence electronic level. Both the $^3\Pi$ and $^1\Sigma^+$ states of AIN have substantial multireference character as noted by the large T_1 diagnostics.⁸ The $^3\Sigma^-$ state does not have substantial multireference character. The dissociation energy for AIN has been measured spectroscopically to be 66 ± 9 kcal/mol.^{19,20} The R/UCCSD(T)/CBS value of 57.3 kcal/mol is consistent with the lower range of

the experimental value. Langhoff *et al.* found the $^1\Sigma^+$ state to be 13.3 kcal/mol above the $^3\Pi$, a few kcal/mol higher than the R/UCCSD(T)/CBS value. In addition, Ebben and ter Mullen²¹ have studied the $C^3\Pi$ state by using laser induced fluorescence.

The diatomic BP has been calculated at the R/UCCSD(T) level² to have a $^3\Pi$ ground state with the $^1\Sigma^+$ 7.36 kcal/mol higher in energy and the $^3\Sigma^-$ state is 20.95 kcal/mol higher in energy for the valence electronic energy. The BP bond energy is substantially higher than the AlN or AlP bond energies.² The multireference character in the three states for BP is like that in AlP. The BP bond energy has been measured to be 82.0 ± 4 kcal/mol based on Knudsen cell measurements in reasonable agreement with the R/UCCSD(T) value of 76.4 kcal/mol.²² Boldyrev and Simons²³ have calculated the ground state of BP to be the $^3\Pi$ with the $^1\Sigma^+$ state 6.8 kcal/mol higher in energy and the $^3\Sigma^-$ state to be 19.7 kcal/mol above the ground state at the QCISD(T)/6-311+G(2df) level which are similar to the higher level R/UCCSD(T) results.

The AIP molecule is very similar to the AlN molecule with the two triplet states essentially isoenergetic and the $^3\Sigma^-$ is the ground state by 0.09 kcal/mol for the valence electronic energy at the R/UCCSD(T)/CBS level. The $^1\Sigma^+$ state is 11.19 kcal/mol higher in energy than the ground state for the valence electronic energy. Although the AIP $^1\Sigma^+$ state does have some multireference character, it is substantially smaller than in BN or AlN. The $^3\Pi$ state for AIP has a small amount of multireference character and the $^3\Sigma^-$ has very little. The dissociation energy for AIP has been measured to be 50.8 ± 3 kcal/mol in excellent agreement with the R/UCCSD(T)/CBS value of 50.7 kcal/mol.²⁴ At the MRCI level with a polarized triple zeta basis set with f functions, Meier *et al.*²⁵ predict the ground state to be the $^3\Sigma^-$ with a T_e of 0.08 eV (1.8 kcal/mol) for the $^3\Pi$ state. Boldyrev and Simons²³ report a T_e of 1.3 kcal/mol at the at the QCISD(T)/6-311+G(2df) level. These apparent differences with the R/UCCSD(T)/CBS value are due to the strong dependence of the state splitting on the basis set. Gomez *et al.*²⁶ report a T_e of 0.108 eV (2.5 kcal/mol) for the $^3\Pi$ state relative to the $^3\Sigma^-$ ground state on the basis of photoelectron spectroscopy measurements although they note that the analysis of the triplet manifold is difficult.

The above results show that there are interesting questions to be answered by full CI calculations in terms of the ground state of the system and how well we are predicting the relative state energies using CCSD(T) which has been extensively used to predict reliable thermodynamic properties.

COMPUTATIONAL APPROACH

We used the triple zeta cc-pVTZ correlation-consistent basis set for this study.⁶ Bond distances, harmonic frequencies, and anharmonic constants for the diatomics were obtained from a fifth order fit of the potential energy surface at the CCSD(T) level. The vibrational quantities are given as supporting information (EPAPS) for completeness.²⁷ The dissociation energy for the $^1\Sigma^+$ state of BN was calculated at

TABLE II. Total energies (a.u.) and state energy differences (kcal/mol) at the CCSD(T) and full CI levels with the cc-pVTZ basis set.

| Molecule | E [CCSD(T)] | E (full CI) | ΔE [CCSD(T)] | ΔE (full CI) | T [CCSD(T)] |
|---------------------|----------------|----------------|----------------------|----------------------|---------------|
| BN($^3\Pi$) | -79.267 167 63 | -79.269 425 8 | 0.0 | 0.0 | 0.0368 |
| BN($^3\Sigma^-$) | -79.225 362 43 | -79.226 902 3 | 26.23 | 26.68 | 0.0158 |
| BN($^1\Sigma^+$) | -79.267 971 87 | -79.267 934 6 | -0.50 | 0.94 | 0.0762 |
| BP($^3\Pi$) | -365.531 778 8 | -365.534 582 0 | 0.0 | 0.0 | 0.0311 |
| BP($^3\Sigma^-$) | -365.501 215 4 | -365.503 498 8 | 19.18 | 19.50 | 0.0198 |
| BP($^1\Sigma^+$) | -365.519 107 8 | -365.522 254 0 | 7.97 | 7.74 | 0.0402 |
| AlN($^3\Pi$) | -296.527 207 3 | -296.530 462 9 | 0.0 | 0.0 | 0.0689 |
| AlN($^3\Sigma^-$) | -296.528 905 5 | -296.530 291 6 | -1.07 | 0.11 | 0.0154 |
| AlN($^1\Sigma^+$) | -296.510 690 7 | -296.511 185 7 | 10.36 | 12.10 | 0.1227 |
| AlP($^3\Pi$) | -582.823 822 2 | -582.826 633 6 | 1.64 | 1.09 | 0.0312 |
| AlP($^3\Sigma^-$) | -582.826 441 4 | -582.828 365 7 | 0.0 | 0.0 | 0.0147 |
| AlP($^1\Sigma^+$) | -582.804 052 9 | -582.807 554 4 | 14.05 | 13.06 | 0.0472 |

the CCSD(T)/complete basis set level as previously described.^{1,2} The open shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree-Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.^{28–30} The CCSD(T) calculations were performed with the MOLPRO suite of programs³¹ on the 144 processor Cray XD-1 at the Alabama Supercomputer Center. The T_2 amplitudes for the open shell molecules were obtained with the program³² NWCHEM on the large HP LINUX cluster at the Molecular Sciences Computing Facility at the Pacific Northwest National Laboratory.

The full CI calculations were done using the efficient $N-2$ resolution full configuration interaction (FCI) algorithms based on the DGEMM computational kernel.⁹ The calculations were done using a parallel vector machine, the 432 MSP Cray-X1 at the Oak Ridge National Laboratory. The full CI calculations consisted of about 45×10^9 determinants for the singlets and about 35×10^9 determinants for the triplets. The full CI calculations were run on the Cray X1E using 128 processors and took about 0.5 h for the 15–20 iterations required to converge to a residual norm of 3×10^{-4} .

RESULTS AND DISCUSSION

The calculated total energies and the state energies are given in Table II. The full CI values are all more negative than the CCSD(T) values except for BN($^1\Sigma^+$) which has a high value for the T_1 diagnostic and which has been shown to have high multireference character. The full CI value is 3.7×10^{-5} a.u. above the CCSD(T) value.

The ground state for BN is predicted to be the $^3\Pi$ at the full CI level in agreement with the MRCI results.^{10,11} With the cc-pVTZ basis set, the $^1\Sigma^+$ state is predicted to be 0.94 kcal/mol above the $^3\Pi$ state. This value lies between the values of Martin *et al.*¹⁰ (1.32 kcal/mol) at the MRCI level with a similar basis set and of Peterson¹¹ (0.54 ± 0.29 kcal/mol) at the CMRCI/CBS level. The latter value is based on values of 0.87 kcal/mol at the CMRCI/CBS level corrected by a value of 0.29 kcal/mol due to the difference between the CMRCI and MRCI results at the cc-pVTZ level. In addition, the CMRCI value at the CBS level is only 0.25 and 0.35 kcal/mol with the cc-pVTZ basis set.

At the CMRCI+ Q /cc-pVTZ level, Peterson¹¹ obtained 0.92 kcal/mol in excellent agreement with our result. Thus, the Q correction to the MRCI results is critical to getting reasonable values for the splitting of the states and the Q correction is apparently accounting for a substantial part of the error in the CMRCI calculations. The full CI results show that the CCSD(T) results with the cc-pVTZ basis set are in error by 1.44 kcal/mol for the energy difference between the $^3\Pi$ and $^1\Sigma^+$ states. We note that there is large T_1 diagnostic for the $^1\Sigma^+$ state consistent with this error in T_e . The T_1 diagnostic for the $^3\Pi$ state is 0.0368 which is about half the value for the $^1\Sigma^+$ state. The difference in the energies for the $^3\Sigma^-$ state as compared to the ground state is only 0.45 kcal/mol between the full CI and CCSD(T) results. The $^3\Sigma^-$ state has a much smaller T_1 diagnostic.

For BP, both methods predict the $^3\Pi$ to be the ground state. The $^3\Sigma^-$ state is the first excited state and full CI predicts it to be 7.74 kcal/mol above the ground state as compared to 7.97 kcal/mol at the CCSD(T) level, a difference of 0.23 kcal/mol. The $^1\Sigma^+$ state is the second excited state and is 19.50 kcal/mol above the ground state at the full CI level and 19.18 kcal/mol higher at the CCSD(T) level, a difference of 0.32 kcal/mol. For these states, the T_1 diagnostics are not that large, with the largest being 0.0402 for the $^1\Sigma^+$ state.

Just as in BN, the full CI and CCSD(T) levels predict a different ground state for AlN. At the full CI level, the $^3\Pi$ state is predicted to be the ground state with the $^3\Sigma^-$ state only 0.11 kcal/mol higher in energy. At the CCSD(T) level, the $^3\Sigma^-$ state is predicted to be the ground state with the $^3\Pi$ state 1.15 kcal/mol higher in energy showing an error in the state energies of 1.26 kcal/mol at the CCSD(T) level. The $^1\Sigma^+$ state is the second excited state and is 12.10 kcal/mol higher at the full CI level and 10.36 kcal/mol higher at the CCSD(T) level, an error at the CCSD(T) level of 1.74 kcal/mol. We note that the $^3\Pi$ and $^1\Sigma^+$ states are characterized by large values of T_1 and should have substantial multireference character. The states characterized by a large T_1 show the largest differences in T_e as compared to the full CI results. Even for the AlN states with large values of T_1 , the difference in the state energies is still less than 2 kcal/mol.

The diatomic AIP is predicted to have a $^3\Sigma^-$ ground state with both methods. The $^3\Pi$ state is the first excited state and full CI predicts it to be 1.09 kcal/mol above the ground state as compared to 1.64 kcal/mol at the CCSD(T) level, a difference of 0.55 kcal/mol. The $^1\Sigma^+$ state is the second excited state and is 13.06 kcal/mol above the ground state at the full CI level and 14.05 kcal/mol higher at the CCSD(T) level, a difference of 0.99 kcal/mol. The T_1 diagnostics are similar in size to those for BP. The T_1 diagnostic for the $^1\Sigma^+$ state is 0.0472 for AIP as compared to 0.0402 for BP, consistent with a larger error in the T_e for this state in the former.

In order to provide more insight into the differences between the full CI values and the CCSD(T) values and the role of the T_1 diagnostic, we also looked at the largest T_2 amplitudes for each state. For the $^1\Sigma^+$ state of BN, the maximum value of the T_2 amplitude is 0.22, consistent with the large T_1 diagnostic and indicative of multireference character. The $^3\Pi$ state of BN had maximum T_2 amplitudes of 0.05 consistent with a single reference state and the $^3\Sigma^-$ had slightly higher maximum T_2 amplitudes of 0.09. For AlN the $^1\Sigma^+$ state had a maximum T_2 amplitude of 0.22, similar to that of $^1\Sigma^+$ BN and consistent with multireference character in the wave function. For the $^3\Pi$ and $^3\Sigma^-$ states, the maximum T_2 amplitude was only 0.09. For BP, the $^1\Sigma^+$ state had a lower maximum T_2 amplitude of 0.13 consistent with a smaller value for the T_1 diagnostic. The $^3\Pi$ state of BP had a maximum value for the T_2 amplitude of 0.10 and the $^3\Sigma^-$ state had a maximum value for the T_2 amplitude of 0.08. The results for the maximum T_2 amplitudes for BP are consistent with the result that the full CI and the CCSD(T) state energy differences are quite similar. For the AIP molecule, the maximum value of the T_2 amplitudes is 0.16. For the $^3\Pi$ state, the maximum value of the T_2 amplitudes is 0.06, and for the $^3\Sigma^-$ state, the maximum value is 0.07. The values of the maximum T_2 amplitudes correlate with the T_1 diagnostics and show that BN and AlN have the most multireference character in the $^1\Sigma^+$ state whereas the BP and AIP have smaller amounts of multireference character in this state as discussed above.

The results show that three of the four molecules are predicted to have a $^3\Pi$ ground state at the full CI/cc-pVTZ level. Only AIP is predicted to have a different ground state $^3\Sigma^-$, but the $^3\Pi$ is only 1.1 kcal/mol higher in energy. The first excited states for BN, AlN, and AIP are predicted to be less than 2 kcal/mol above the ground state and are predicted to be the $^1\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$, respectively. Only for BP is a substantial splitting between the ground state and first excited state of ~ 8 kcal/mol predicted. An interesting result is the destabilization of the $^1\Sigma^+$ state with increasing atomic number. Only for BN is the $^1\Sigma^+$ state of low energy. For the remaining molecules, this state is the highest energy state of the three lowest states.

The fact that the $^3\Pi$ state is the lowest energy state for three of the four molecules and is only 1.1 kcal/mol above the $^3\Sigma^-$ state for BP suggests that the σ and π orbitals formed from the valence p orbitals are approximately degenerate in a simple molecular orbital picture. Thus in simple molecular orbital diagrams for diatomics,³³ one should draw these orbitals as being approximately degenerate with the

state energy differences depending on whether there are two electrons in each orbital or three electrons in the π orbital and one in the σ orbital. There is no evidence based on the state energies for placing the π orbital below the σ orbital and putting four electrons in the π orbital as the ground state for these diatomics. Only in BN does this configuration have an energy comparable to the ground state.

Further information about this simple model is provided by the orbital ordering in terms of the initial spin restricted Hartree-Fock orbitals. The orbital energies are given as supporting information (EPAPS).²⁷ The $^1\Sigma^+$ state for all of the diatomics has the π orbital (derived from the valence p orbital) lying below the σ orbital (derived from the valence p orbital) as expected. This is consistent with the inversion between the σ and π orbitals noted in many textbooks³³ and arises from the interaction of the σ orbital from the valence p orbital with the σ^* orbital from the valence s orbital which is close in energy. The splitting between the σ and π orbitals is small for all of the molecules with the largest gap found for BP. For AlN, the π orbital is approximately degenerate with the σ^* orbital composed of the valence s orbitals.

The orbital orderings for the open shell states exhibit a more complicated pattern. For BN ($^3\Pi$), the singly occupied σ and π orbitals are nearly degenerate in energy, with the σ orbital being slightly more stable and the doubly occupied π orbital higher in energy than either singly occupied orbital. For BN ($^3\Sigma^-$), the π orbital is lower in energy than the doubly occupied σ orbital. Although BP ($^3\Pi$) has an orbital pattern similar to BN ($^3\Pi$), BP ($^3\Sigma^-$) has the σ orbital more stable than the π orbital. For the AlN ($^3\Pi$), the σ^* orbital formed from the valence s orbitals is higher in energy than the doubly occupied π orbital (derived from the valence p orbitals). Both singly occupied σ and π orbitals were higher in energy. The orbital energy profile for AlN ($^3\Sigma^-$) is similar to that of BP ($^3\Sigma^-$). For AIP ($^3\Pi$), the singly occupied π orbital is slightly lower in energy than the σ orbital and both were lower in energy than the doubly occupied π orbital. AIP ($^3\Sigma^-$) has an orbital pattern similar to that of BN ($^3\Sigma^-$). Meier *et al.*²⁵ suggest that the σ^* orbital formed from the valence s orbitals and the σ orbital formed from the valence p orbitals become stabilized relative to the π orbital formed from the valence p orbitals. This leads to the $\sigma^2\pi^2$ electron configuration being stabilized and the π^4 being destabilized with respect to $\sigma^1\pi^3$. This is also consistent with our simple model and the state orderings.

There are other factors which also play a role in the ordering of the states. The bond distances for the three states (see Table III) increase in the order $r_e(^1\Sigma^+) > r_e(^3\Pi) > r_e(^3\Sigma^-)$ with substantial differences in the bond distance for each state. As the atoms get heavier, the difference in the bond distances between the $^1\Sigma^+$ and $^3\Pi$ states gets larger. In a simple model, the $^1\Sigma^+$ state has a triple bond, the $^3\Pi$ state a double bond, and the $^3\Sigma^-$ state a single bond. Following Peterson,¹¹ for BN, the $^3\Pi$ ground state correlates with the ground state atoms and the $^1\Sigma^+$ state correlates with the ground state of B and the first excited state of N. Near r_e , the $^1\Sigma^+$ state correlates with the excited state of B and the ground state of N to give a stronger bond, but this interaction has to be balanced by the promotion energy. The $^3\Sigma^-$ state

TABLE III. CCSD(T)/cc-pVTZ bond distances.

| Molecule | R_e (Å) |
|---------------------|-----------|
| BN($^3\Pi$) | 1.3358 |
| BN($^3\Sigma^-$) | 1.4851 |
| BN($^1\Sigma^+$) | 1.2740 |
| BP($^3\Pi$) | 1.7595 |
| BP($^3\Sigma^-$) | 1.9730 |
| BP($^1\Sigma^+$) | 1.6876 |
| AlN($^3\Pi$) | 1.8108 |
| AlN($^3\Sigma^-$) | 1.9324 |
| AlN($^1\Sigma^+$) | 1.6850 |
| AIP($^3\Pi$) | 2.2331 |
| AIP($^3\Sigma^-$) | 2.4322 |
| AIP($^1\Sigma^+$) | 2.1081 |

also correlates with the ground state atoms. The excited state transitions for the atoms,³⁴ which represent to first order a promotion energy, are: (for B) $^2P^0 \rightarrow ^4P$ at 82.3 kcal/mol (for Al), $^2P^0 \rightarrow ^2S$ at 72.4 kcal/mol, and (for N and P) $^4S^0 \rightarrow ^2D^0$ at 54.9 and 32.5 kcal/mol. For Al, the second excited state, $^2P^0 \rightarrow ^4P$ is at 82.9 kcal/mol. Thus, one would expect similar behavior in terms of the energetics for the B and Al atoms, but there is a clear difference for the promotion energy of the N and P atoms.

For BN, the ground state is the $^3\Pi$ and the $^1\Sigma^+$ is approximately degenerate due to a balance in the promotion energy and the additional π bonding. The state with the longest bond is the $^3\Sigma^-$ state which is the highest in energy. In the simplest molecular orbital picture, the $\pi^4\sigma^0$ and the $\pi^2\sigma^2$ configurations are thus comparable in energy. For BP, the bond distances are substantially longer than those in BN consistent with bonding between first and second row atoms. The bonding interaction is weaker due to lower overlaps so the energies of the states are closer to each other. The energy of the $^1\Sigma^+$ state is not stabilized as much by the additional π bonding, so the promotion energy is more important and the energy difference between the $^3\Pi$ state and the $^1\Sigma^+$ state increases. For AlN, the amount of π bonding is small and the $^3\Sigma^-$ state is only slightly higher in energy than the $^3\Pi$ ground state. The weaker π overlap cannot overcome the promotion energy, so the $^1\Sigma^+$ is destabilized even more so than in BP. For AIP, there is very weak π bonding due to the long bond distances and poor overlap commonly found in π bonds between second row atoms, so the $^3\Sigma^-$ state actually becomes the ground state although the $^3\Pi$ state is very close in energy. The $^1\Sigma^+$ state gains very little in terms of π bonding and cannot overcome even the lower promotion energy on P, so it is even higher in energy relative to the ground state. Thus the state orderings are consistent with simple orbital models and considerations of π bond energies and atomic orbital promotion energies.

The valence electronic dissociation energies with the cc-pVTZ basis set for the diatomic ground state at the full CI level are given in Table IV. The CCSD(T) values are always lower than the full CI values by 0.67, 0.61, 1.00, and 0.06 kcal/mol for BN, BP, AlN, and BP, respectively. With

TABLE IV. Electronic dissociation energies D_e in kcal/mol.

| Molecule | D_e [CCSD(T)] | D_e (full CI) |
|---------------------|-----------------|-----------------|
| BN($^3\Pi$) | 97.14 | 97.18 |
| BP($^3\Pi$) | 71.01 | 71.63 |
| AlN($^3\Pi$) | 51.29 | 52.59 |
| AIP($^3\Sigma^-$) | 46.90 | 46.96 |

this basis set, the electronic contribution to the dissociation energy is still 5–6 kcal/mol away from the CBS limit (compare values in Tables I and IV).

CONCLUSIONS

Full CI calculations on the group-III A–group-VA diatomic molecules BN, BP, AlN, and AIP show that the R/UCCSD(T) method is good to substantially better than 1 kcal/mol when the T_1 diagnostic for the CCSD(T) calculation is small. For large T_1 values, the CCSD(T) method is good to better than 2 kcal/mol. The ground state for all of these diatomics except for AIP is predicted to be the $^3\Pi$, and for AIP the $^3\Sigma^-$ state is predicted to be the ground state with the $^3\Pi$ state very close in energy. The state energies can be rationalized from simple bonding pictures and molecular orbital concepts. The calculations show that there is little evidence for placing the π orbital below the σ orbital in terms of the ground state of these heteronuclear diatomic molecules.

ACKNOWLEDGMENTS

We thank Professor K. A. Peterson for many helpful discussions. Funding is provided in part by the Department of Energy, Office of Energy Efficiency and Renewable Energy under the Hydrogen Storage Grand Challenge, Solicitation No. DE-PS36-03GO93013. The Robert Ramsay Fund of the University of Alabama is thanked for support. Part of this work was done as part of the Chemical Hydrogen Storage Center. This work is supported in part by the Scientific Discovery through Advanced Computing (SciDAC) program of the U.S. Department of Energy, the Division of Basic Energy Science, Office of Science, using the resources of the National Center for Computational Sciences at Oak Ridge National Laboratory under Contract No. DE-AC05-00OR22725. This research was performed in part using the computational facilities at the Alabama Supercomputing Center. Part of this research was performed using the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) at the PNNL. The EMSL is a national user facility funded by the Office of Biological and Environmental Research in the U.S. Department of Energy. PNNL is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy.

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