A coupled cluster study of As2

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Theoretical calculations at the self-consistent field (SCF) and coupled-cluster method including all single and double excitations (CCSD) have been carried out for As₂. A variety of basis sets employing both segmented contractions and atomic natural orbitals have been developed and investigated. The predicted equilibrium bond length ($r_e = 2.107$ Å), harmonic vibrational frequency ($\omega_e = 447$ cm^{-1}), and ionization potentials (9.75, 10.08, and 14.78 eV) are in excellent agreement with experimental values 2.103 Å, 430 cm^{-1}, and 9.89 eV, 10.22 eV, and 15.32 eV; respectively. The best theoretical estimates for the dissociation energy (71.6 kcal/mol) and for the electron affinity (0.56 eV) were obtained at the CCSD level of theory employing large basis sets. However, given the importance of correlation effects on these two properties (the corresponding SCF values are 12.4 kcal/mol and 0.42 eV), the theoretical predictions could substantially be affected by the inclusion of connected triple excitations not considered in this work. The open-shell atomic As(^4S) and diatomic calculations for As₂⁺ and As₂⁻ were carried out using a recently developed CCSD program that is based on restricted Hartree–Fock references and does not include any spin contamination for the correlation energies. The importance of correlating 3d electrons and the basis-set superposition error for D_e are analyzed. The effect of including d- and f-type polarization functions in the basis set is also discussed.

INTRODUCTION

Small arsenic clusters have recently been observed in supersonic beams of semiconductor clusters obtained by laser vaporization of pure GaAs[1-3]. In particular, As₂ has been the subject of a considerable number of experimental investigations in the past[4-6]. The photoelectron spectrum of As₂ has recently been recorded,[6] and the spectroscopic constants of the ground state $^1\Sigma_g^+$ are also well known[4].

Diatomic arsenic has also been the focus of a number of theoretical calculations.[7-12] Kok and Hall[8] studied the dissociation energies for group 5A diatomics including As₂ using the generalized molecular-orbital theory. Watanabe, Sakai, and Kashiwagi[9] presented results for the spectroscopic constant of As₂ obtained at the self-consistent-field (SCF) level of theory including a model potential for the inner-shell nonvalence electrons. More recently, Balasubramanian[11] has studied the spectroscopic properties of As₂ using complete active space (CASSCF/FOCI) calculations with effective core potentials, and Andzelm, Russo, and Salahub[12] reported spectroscopic constants and ionization potentials for As₂ based on localized density-functional calculations.

In this work, a detailed theoretical study of As₂ will be presented. For the first time, results of spectroscopic constants (r_e, ω_e, and D_e), ionization potentials, and the electron affinity of the $^1\Sigma_g^+$ ground state, are obtained at a highly correlated level of theory based on all-electron SCF wavefunctions using large primitive Gaussian basis sets. A variety of basis sets employing both segmented and generalized contractions based on correlated atomic natural orbitals (ANO) have been developed and investigated. Using the coupled-cluster method including all single and double excitations (CCSD), correlation effects on the equilibrium bond

length, vibrational frequency, and dissociation energy of As₂ are presented. In particular, the role of 3d-electron correlation effects is analyzed. The importance of d- and f-type polarization functions and the magnitude of basis-set superposition error corrections for the dissociation energy both at the SCF and CCSD levels of theory are discussed in detail.

BASIS SETS FOR As

The basis sets that utilized segmented contractions are based on Dunning's 14s11p5d Gaussian primitive set.[13] Several contraction schemes for this primitive set were analyzed, but only results obtained with three of them will be presented in this paper. The smallest of the segmented contractions is based on a (82211-6311-5) contraction scheme and will be denoted as ⟨541⟩. The other two segmented contractions employed in this work, (6112211-61211-5) and (6112211-61211-41), are more flexible in the s-p region and were suggested by Grev[14] to the present author. They are of approximate double-ζ quality and will be indicated as ⟨751⟩ and ⟨752⟩, respectively. Contraction coefficients were obtained from uncontracted SCF calculations on As(^4S). These basis sets were supplemented with a d-type polarization functions of exponent α_d(As) = 0.25 (indicated as + P in the following).

The atomic natural orbitals (ANO) basis sets originate from two different primitive sets and were constructed following Almlöf and Taylor's[15] procedure. The first set of ANO is based on Dunning's 14s11p5d primitive set augmented with the above-mentioned polarization function. An ANO basis set including 6s, 5p, and 3d functions will be denoted as [653], for example. Atomic natural orbitals were obtained from atomic As(^4S) configuration-interaction calculations including all single and double excitations (CISD)

from the $n = 3$ and $n = 4$ shells. In one particular case, ANO were generated from a valence ($n = 4$) CISD calculation. The resulting basis set, [653]val, includes all natural orbitals with occupation numbers bigger than 10^{-5}. When correlation effects from the $n = 3$ shell were included, the resulting [653] and [764] basis sets employed in this work included all natural orbitals with occupation numbers larger than 10^{-3} and 10^{-4}, respectively.

The second primitive set is Partridge's $21s16p10d$ orbital basis[16] augmented with three d and five f functions to improve the description of the polarization region. For this primitive set consisting of 169 basis functions, the additional d- and f-function exponents were chosen as α_d(As) = 0.18, 0.09, 0.045; and α_f(As) = 1.5625, 0.625, 0.25, 0.10, 0.04. Contraction coefficients for this primitive set were obtained from an atomic CI calculation including all single and double excitations from the $n = 3$ and $n = 4$ shells. The only contraction employed in this work, [7642], consists of 59 basis functions and includes all natural orbitals with occupation numbers larger than 10^{-4}.

An additional f-type function was included (indicated as $+f$ in the following) with the $\langle 752 \rangle + P$ and [764] basis sets obtained from the smaller $15s11p5d + P$ primitive set. The chosen exponent for the r_e, ω_e, and D_e calculations was α_f(As) = 1.25. A more diffuse exponent [α_f(As) = 0.25] was also employed for the electron affinity and ionization potential predictions. Although the optimum value (in an energetic sense) for α_f(As) at the SCF level of theory is close to 0.25, it was observed that when correlation effects are included (specially from $3d$ electrons), the optimum f exponent is much closer to 1.25. Only the pure spherical components of the d- and f-type functions have been included in all basis sets employed in this study.

THEORETICAL APPROACH

All-electron SCF calculations were carried out with the above described basis sets. Correlation effects were based upon coupled-cluster theory including all single and double excitations (CCSD)[17,18]. The As $1s$, $2s$, and $2p$ orbitals were kept doubly occupied in all correlated calculations whereas the $3s$, $3p$, and $3d$ orbitals were selectively kept active or inactive (double occupied) in all configurations. The active shells will be indicated with numbers in parentheses following the theoretical method used, i.e., CCSD(3,4) or CCSD(4). For closed-shell situations the programs employed are based on the recent reformulation of the CCSD equations[19]. These codes as well as another efficient vectorized CCSD program[20] are capable of handling very large configuration spaces. To locate equilibrium structures, analytic energy gradient methods were employed both at the SCF (Ref. 21) and CCSD (Ref. 22) levels of theory with the segmented basis sets. Harmonic vibrational frequencies were obtained by finite differences of analytic energy gradients. For the ANO basis sets, equilibrium bond lengths and harmonic frequencies were calculated by finite differences of energies. The errors bars in the theoretical predictions due to numerical differentiation were kept smaller than 10^{-3} Å and 1 cm^{-1}, respectively. The atomic As and open-shell CCSD calculations for As₂ were carried out using a recently

developed program for open-shell CCSD wave functions based on restricted Hartree–Foch (RHF) references.[23] The open-shell CCSD energies are fully spin adapted, i.e., they are based on open-shell RHF references and do not include any spin contamination at the correlated level. The As₂ SCF calculations with the large uncontracted $21s16p13d\ 5f$ primitive basis set were carried out with the direct SCF program TURBOMOLE.[24] All calculations were performed on a MIPS M-2000 superminicomputer and a MIPS RS2030 workstation.

EQUILIBRIUM BOND LENGTH, VIBRATIONAL FREQUENCY, AND ENERGIES

Results obtained for the equilibrium bond length, vibrational frequency, and energy of As₂ with various segmented and ANO basis sets are presented in Table I.

The $\langle 541 \rangle + P$ basis set is evidently too contracted to describe As₂ accurately. Both at the SCF and CCSD levels of theory, r_e and ω_e, do not compare favorably with the more reliable results obtained with larger basis sets. The SCF and CCSD equilibrium bond lengths are short by ~ 0.02 Å and the vibrational frequencies are off by ~ 20–24 cm^{-1}. The agreement between the predicted CCSD(3,4) r_e value and the experimental result is obviously fortuitous and due to cancellation of remaining basis set and correlation errors. The other two segmented basis sets employed in this work ($\langle 751 \rangle + P$ and $\langle 752 \rangle + P$) are of roughly double-ζ plus polarization quality. Both of them give quite satisfactory results. The additional flexibility for the $3d$ electrons of the $\langle 752 \rangle + P$ basis compared to the $\langle 751 \rangle + P$ basis is evident at the CCSD level of theory. A comparison of bond lengths obtained with these two basis sets shows that the former are shorter by ~ 0.01 Å. The changes in equilibrium bond length and vibrational frequency with the $\langle 752 \rangle + P$ basis set due to correlation effects at the CCSD level of theory are quite important but in line with what is usually obtained for triplebonded molecules like N₂. A breakdown of the $n = 3$ shell correlation effects for this basis set clearly indicates that the $3d$ electrons are responsible for most of the changes due to inclusion of this shell in the active space. Comparing results obtained at the CCSD(4) and CCSD(3,4) levels of theory, it is found that the bond length is shortened by 0.009 Å, and the harmonic frequency is increased by 5 cm^{-1}.

The next two entries in Table I correspond to the results obtained with two ANO basis sets of the same size, based on atomic CISD calculations including and excluding correlation effects from the $n = 3$ shell, with exactly the same primitive set. These are labeled [653] and [653]val, respectively. It is interesting to note that the two sets of results are practically the same except for the expected differences in the total energies due to basis-set construction.

Comparison of the [653] and [764] basis with the uncontracted $15s11p5d + P$ basis set results at the SCF level of theory indicate that the overall quality of the ANO results is extremely good. Addition of an f function to the [764] basis set leads to a further shortening of the equilibrium bond length. The [764] $+f$ predictions at the CCSD (3,4) level of theory, 2.107 Å and 447 cm^{-1}, are in excellent agreement with the experimental values 2.103 Å and 430 cm^{-1}. With

TABLE I. Theoretical predictions obtained for As_2 with various basis sets at the SCF and CCSD levels of theory.

Basis set	Method	r_e (Å)	ω_e (cm^{-1})	E (hartrees)[a]
$\langle 541 \rangle + P$	SCF	2.040	538	0.773 35
	CCSD (4)	2.106	456	0.947 95
	CCSD (3,4)	2.102	461	0.985 91
$\langle 751 \rangle + P$	SCF	2.069	514	0.022 50
	CCSD (4)	2.142	437	0.240 47
	CCSD (3,4)	2.136	439	0.359 84
$\langle 752 \rangle + P$	SCF	2.064	514	0.026 86
	CCSD (4)	2.132	436	0.252 86
	CCSD (3d,4)	2.122	440	0.499 57
	CCSD (3,4)	2.123	441	0.702 26
[653] val	SCF	2.064	514	0.353 58
	CCSD (4)	2.130	437	0.583 61
	CCSD (3,4)	2.124	440	0.949 66
[653]	SCF	2.063	514	0.349 85
	CCSD (4)	2.132	435	0.574 12
	CCSD (3,4)	2.126	440	1.305 64
[764]	SCF	2.064	514	0.353 22
	CCSD (4)	2.130	437	0.581 87
	CCSD (3,4)	2.124	441	1.371 61
Uncontracted $15s11p5d + P$	SCF	2.064	514	0.353 68
[764] $+f$	SCF	2.059	514	0.354 76
	CCSD (4)	2.122	439	0.589 59
	CCSD (3,4)	2.107	447	1.498 03
Uncontracted $21s16p13d\,5f$	SCF	2.059	513	0.499 27
Experimental[b]		2.103	430	

[a] Energies are reported in hartrees as $-(E + 4459$ hartrees) for the $\langle 541 \rangle + P$ basis and as $-(E + 4468$ hartrees) for all the other basis sets.
[b] Reference 4.

this basis set, the CCSD (3,4) wave function contains 172 212 configuration state functions in D_{2h} symmetry. In order to test the completeness of the [764] $+f$ basis set, an SCF calculation was carried out with the larger $21s16p13d\,5f$ uncontracted primitive set. The results obtained ($r_e = 2.059$ Å and $\omega_e = 513$ cm^{-1}), indicate that the [764] $+f$ results ($r_e = 2059$ Å and $\omega_e = 514$ cm^{-1}) are very close to the expected basis-set limit. As mentioned above, the changes in r_e and ω_e due to correlation effects may be viewed as somewhat larger than expected. For comparison purposes, it is interesting to note that the change in r_e for N_2 from SCF to CCSD with a DZP basis set is $+ 0.038$ Å. The predicted changes in As_2 for r_e and ω_e are $+ 0.048$ Å and $- 67$ cm^{-1} ([764] $+f$), and $+ 0.059$ Å and $- 63$ cm^{-1} ($\langle 752 \rangle + P$).

DISSOCIATION ENERGY

Atomic energies for As(^4S) calculated at the SCF, CISD, CISD + Davidson's correction (CISD + Q), and CCSD levels of theory are presented in Table II. The CI results were obtained using the shape-driven graphical unitary group approach CI program,[25] and the CC results were obtained with a recently developed program[23] briefly described in a previous section. It is interesting to note that all the CCSD(4) energies lie between the CISD(4) and

CISD(4) + Q (Davidson's corrected[26]) values and are much closer to CISD(4) than to CISD(4) + Q. However, when correlation effects from the $n = 3$ shell are included, the CCSD(3,4) energies indicate that the Davidson's correction underestimates the effect of quadruple excitations. This observation is in agreement with previous results in molecules with a large number of active electrons.[27–29] As mentioned above, the ANO basis sets are constructed from the eigenvectors of the CISD one-particle density matrix. To

TABLE II. Atomic As(^4S) energies at the SCF, CISD, CISD + Davidson's correction (CISD + Q), and CCSD levels of theory.[a]

Method	Basis set			
	$\langle 752 \rangle + P$	[764]	[764] $+f$	[7642]
SCF	0.004 09	0.168 47	0.168 47	0.238 37
CISD(4)	0.075 57	0.241 12	0.248 20	0.322 79
CISD(4) + Q	0.079 11	0.244 64	0.252 16	0.326 99
CCSD(4)	0.076 33	0.241 88	0.249 31	0.323 99
CISD(3,4)	0.284 18	0.608 99	0.617 58	0.772 68
CISD(3,4) + Q	0.298 64	0.630 82	0.640 68	0.801 91
CCSD(3,4)	0.299 87	0.637 30	0.647 13	0.808 39

[a] Energies are reported in hartrees as $-(E + 2234$ hartrees).

obtain the CCSD natural orbitals an energy gradient calculation, which is not presently available for open-shell situations, would be required.[22] However, it is reasonable to assume that CISD and CCSD ANO will give similar qualitative results. At the CISD level of theory, the [764] and [7642] ANO are both capable of recovering 96% of the total atomic CISD correlation energy available in the respective uncontracted calculations.

Theoretical predictions for the dissociation energy at the SCF and CCSD levels of theory are presented in Table III. These results clearly demonstrate the importance of correlation effects for D_e. With the $\langle 752 \rangle + P$ basis set the predicted dissociation energies are 11.7, 62.9, and 64.3 kcal/mol at the SCF, CCSD(4), and CCSD(3,4) levels of theory, respectively. The CCSD correlation contributions to the dissociation energy of As₂ are of significant and similar magnitude for all basis sets employed in this work.

For the $\langle 752 \rangle + P$ basis and the [764] ANO, the basis-set superposition error (BSSE) was estimated using the counterpoise method. To this effect, atomic As calculations were carried out in the presence of a dummy atom at the optimized As₂ equilibrium bond length for each particular level of theory. The BSSE corrections are given in parentheses in Table III and should be substracted from the calculated D_e values. At all levels of theory, the BSSE corrections are smaller for the ANO [764] basis than for the segmented $\langle 752 \rangle + P$ basis set. For both basis sets the BSSE correction becomes larger with the number of correlated electrons. At the CCSD (3,4) level of theory a correction of 2.6 kcal/mol is obtained with the [764] basis, whereas at the SCF level the correction is only 0.3 kcal/mol. After substracting the BSSE, the calculated D_e with the $\langle 752 \rangle + P$ basis are 59.8 kcal/mol [CCSD(4)] and 58.8 kcal/mol [CCSD(3,4)]. The corresponding figures with the [764] basis are 59.7 and 57.3 kcal/mol, respectively. A negative electron-correlation contribution from the $n = 3$ shell is found with both basis sets.

TABLE III. Theoretical predictions for the dissociation energy (in kcal/mol) of the reaction $As_2(^1\Sigma_g^+) \rightarrow As(^4S) + As(^4S)$. BSSE corrections are given in parentheses for the $\langle 752 \rangle + P$ and [764] basis sets.

Basis set	SCF	CCSD(4)	CCSD(3,4)
$\langle 751 \rangle + P$	10.0	61.5	64.4
$\langle 752 \rangle + P$	11.7 (1.5)	62.9 (3.1)	64.3 (5.5)
[764]	10.2 (0.3)	61.6 (1.9)	60.9 (2.6)
Uncontracted 15s11p5d + P	10.5	···	···
[764] + f	11.2	63.6	63.0
[7642][a]	12.4	70.4	71.6
Uncontracted 21s16p13d 5f	14.1	···	···
Experimental[b]			91.3

[a] Upper bounds to D_e obtained at $r = 2.059$ Å (SCF) and $r = 2.107$ Å (CCSD).
[b] Reference 4.

The dissociation energy obtained with the [764] basis at the SCF level (10.2 kcal/mol) is in good agreement with the uncontracted result (10.5 kcal/mol). Addition of an uncontracted f function to the [764] basis set gives dissociation energies at the CCSD level of theory that are approximately 2 kcal/mol larger than the [764] values. However, with use of the [7642] ANO basis set (obtained from the $21s15p13d\,5f$ primitive set) an important change in the dissociation energy is observed at the CCSD level of theory. The values obtained for D_e are 11.5, 70.4, and 71.6 kcal/mol with the SCF, CCSD(4), and CCSD(3,4) methods, respectively. No reoptimization of the As₂ equilibrium bond length was attempted with the [7642] basis set. These figures were calculated at $r = 2.059$ Å (SCF) and $r = 2.107$ Å (CCSD), the optimized bond lengths with the [764] + f basis, and should therefore be viewed as upper bounds to the true D_e values. With use of the uncontracted $21s16p13d\,5f$ primitive set, the predicted SCF D_e is 14.1 kcal/mol compared to the estimated 12.4 kcal/mol obtained with the [7642] basis set.

Results presented in Table III clearly demonstrate the difficulties inherent in the *ab initio* determination of dissociation energies[30]. Both basis set and correlation effects need to be carefully converged if accurate predictions of dissociation energies are sought. In the case under study, the 19.7 kcal/mol difference between the experimental value (91.3 kcal/mol) and the best theoretical prediction in this paper (71.6 kcal/mol) may partially be attributed to remaining correlation and basis set errors in the theoretical calculation.

IONIZATION POTENTIALS AND ELECTRON AFFINITY

The ionization potentials (IPs) of As₂ are experimentally known[6] and the electron affinity (EA) has also been estimated[5]. From a theoretical point of view, electron affinities are more difficult to predict than ionization potentials due to the importance of correlation and basis set effects, especially on the negative charged species. A theoretical study of atomic $As^-(^3P)$, $As(^4S)$, and $As^-(^3P)$ energies based on the $\langle 752 \rangle + P$ basis set, indicate that additional s and p diffuse functions are essential to properly describe $As^-(^3P)$. In this work, two sets of s and two sets of p functions, both with exponents 0.03 and 0.01, were added to the previously described $\langle 752 \rangle + P$ basis set. These exponents were chosen following an even-tempered criterium. The resulting basis set is indicated as $\langle 752 \rangle + P + \text{diff}(2s,2p)$. Results obtained with this basis set were compared at the SCF level of theory with uncontracted $14s11p5d + P + \text{diff}(2s,2p)$ values, and the contraction errors for the atomic IPs and EA were found to be smaller than 0.01 eV. Results obtained for the EA and three IPs of As₂ with this basis set at the SCF and CCSD levels of theory are presented in Table IV. Results obtained with an additional f function are also presented in Table IV. All CCSD calculations were carried out with the 10 lowest molecular orbitals (corresponding to the atomic $n = 1,2$ shells) and their virtual counterparts frozen. All calculations in Table IV were carried out at the experimental (2.103 Å) geometry.

In general, the predicted IPs are in good agreement with

TABLE IV. Vertical ionization potentials and electron affinity as As$_2$ as predicted by the SCF and CCSD methods.

Molecule and state	Method	Basis set			
		$\langle 752 \rangle + P + 2\,\text{diff}(s,p)$		$\langle 752 \rangle + P + 2\,\text{diff}(s,p) + f$	
		E (hartrees)[a]	ΔE (eV)	E (hartrees)[a]	ΔE (eV)
As$_2(^1\Sigma_g^+)$	SCF	1.030 65	$\cdots$	1.035 56	$\cdots$
	CCSD	1.545 33	$\cdots$	1.584 94	$\cdots$
As$_2^-$ $(^2\Pi_g)$	SCF	1.045 74	0.41	1.051 17	0.42
	CCSD	1.560 06	0.40	1.606 69	0.59
As$_2^+$ $(^2\Pi_u)$	SCF	0.709 85	8.73	0.715 69	8.70
	CCSD	1.191 09	9.64	1.226 57	9.75
	expt.[b]				9.89
As$_2^+$ $(^2\Sigma_g^+)$	SCF	0.671 26	9.78	0.678 42	9.71
	CCSD	1.177 86	10.00	1.214 44	10.08
	expt.[b]				10.22
As$_2^+$ $(^2\Sigma_u)$	SCF	0.443 75	15.97	0.449 32	15.95
	CCSD	1.011 85	14.52	1.041 77	14.78
	expt.[b]				15.32

[a] Energies are reported in hartrees as $-(E + 4467\ \text{hartrees})$.
[b] Reference 6.

the experimental data. The CCSD values are generally closer to the experimental values than the SCF ones, except for the $^1\Sigma_g^+ \rightarrow {}^2\Sigma_u$ ionization process where the contribution from correlation effects is found to be negative. Inclusion of an f function with exponent 0.25 does not change the overall picture, although one of the IPs is increased by as much as 0.26 eV.

For the electron affinity, the inclusion of the same f function at the CCSD level of theory gives an important relative change of 0.19 eV, whereas the SCF value is almost not affected. This effect is not observed if $\alpha_f(\text{As}) = 1.25$ is used. In this case, the values obtained for the EA with the SCF and CCSD (3,4) methods were 0.42 and 0.44 eV, respectively. In view of the importance of diffuse functions for the correct description of As$_2^-$ $(^2\Pi_g)$, a second set of polarization d functions with exponent $\alpha_d(\text{As}) = 0.064$ was added to the basis set. The predicted EA with this $\langle 752 \rangle + 2P + \text{diff}(2s,2d) + f$ basis set was 0.42 eV (SCF) and 0.56 eV (CCSD). The last figure is the best theoretical estimate for the EA presented in this work. The experimental value of the EA of As$_2$ (0.10 ± 0.18 eV) (Ref. 5) is not in agreement with the present theoretical prediction.

CONCLUDING REMARKS

Previous theoretical calculations on As$_2$ had been all carried out using lower levels of theory. Watanabe, Sakai, and Kashiwagi[9] obtained $r_e = 2.138$ Å and $\omega_e = 453\ \text{cm}^{-1}$ using a model potential at the SCF level of theory. Balasubramanian's[11] results for As$_2$ ($r_e = 2.164$ Å and $\omega_e = 394$ cm^{-1}) were obtained with the CASSCF/FOCI method employing effective core potentials.

The theoretical predictions presented in this work ($r_e = 2.107$ Å and $\omega_e = 447\ \text{cm}^{-1}$) are in excellent agreement with the experimental values: 2.103 Å and 430 cm^{-1}. In

order to obtain these results it has been necessary to include f-type functions in the basis set and to take into account correlation effects (including $3d$ electrons) at a much higher level of theory (CCSD) than those previously used by other authors. However, even with the modest $\langle 752 \rangle + P$ basis set, the CCSD predictions without including $3d$-electron correlation ($r_e = 2.132$ Å and $\omega_e = 436\ \text{cm}^{-1}$) are in good qualitative agreement with the experimental data.

The important difference (19.1 kcal/mol) between the calculated and experimental D_e maybe partially attributed to higher correlation effects (most importantly connected triple excitations) not considered in the present work. The effect of triple excitations may also be crucial on the calculated electron affinity, and no definite claim on the theoretical predictions for D_e and EA should be made before this effect is taken into account.

Finally, it is worth emphasizing that the $\langle 751 \rangle + P$ and $\langle 752 \rangle + P$ basis sets employed in this work give quite remarkable results for As$_2$, both at the SCF and CCSD levels of theory. Given the moderate size of these bases (32 and 37 basis functions, respectively) it is realistic to say that much larger third-row compounds will soon be the focus of theoretical calculations of similar quality as those presented herein.

ACKNOWLEDGMENTS

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