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Accurate ab Initio Structural Parameters of the Diatomic and Triatomic van der Waals Molecules ^{11}BNg ($X^2\Pi$, $A^2\Sigma^+$) and ^{11}BNg$_2$ ($\tilde{X}^2B_1$), Ng = ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr, and ^{132}Xe

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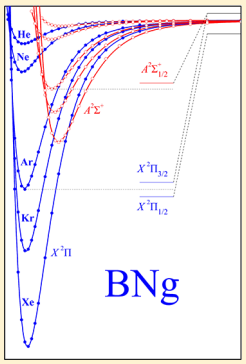
ABSTRACT: The weakly interacting BNg and BNg$_2$ molecular systems, Ng = He, Ne, Ar, Kr, and Xe, have been thoroughly studied through coupled-cluster RCCSD(T) calculations and large correlation consistent basis sets. For the BNg diatomics, the states examined are the $X^2\Pi$ and $A^2\Sigma^+$, and the $\tilde{X}^2B_1$ state for the C_{2v} BNg$_2$ triatomics. A series of corrections render our final results reliable, judging as well from the (limited) experimental numbers available. Both BHe and BHe$_2$ are marginally unbound, whereas the attractive interactions of the BNg $X^2\Pi$ states, where Ng = Ne, Ar, Kr, and Xe, are D_0 = 19.8, 98.2, 141.9, and 209.1 cm^{-1}, respectively. For the BRn (Rn = radon) species, an estimated value of interaction energy $D_0 \approx 280$ cm^{-1} is obtained by a D_0 versus static polarizability (α) extrapolation. Corresponding atomization energies of the BNg$_2$ ($\tilde{X}^2B_1$) molecules are AE_0 = 52.0 (BNe$_2$), 263.4 (BAr$_2$), 384.6 (BKr$_2$), and 576.9 (BXe$_2$) cm^{-1}.



1. INTRODUCTION

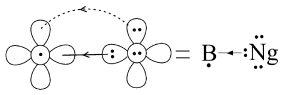
Not so many years ago, we have published a series of very accurate theoretical papers on the electronic structure of the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of the lithium-noble gas diatomics, LiNg, where Ng = He, Ne, Ar, and Kr.[1−3] With respect to the first excited state of Li*(^{2}P;1s^{2}2p^1), 1.848 eV above the ground ^{2}S state,[4] the calculated binding energies of the $A^2\Pi$ states of the LiNg species are $D_0 = D_e - (\omega_e/2) + (\omega_e x_e/4)$ = 842.6,[1] 164.8,[2] 794.6,[3] and 1129.0[3] cm^{-1} for Ng = He, Ne, Ar, and Kr, respectively. Recall that the ^{2}P(2p^1) state of the Li atom is "isovalent" to the ground ^{2}P(2s^{2}2p^1) state of the B atom. Therefore, the Boron−Ng interactions are expected to be of similar nature to those of Li*(^{2}P)−Ng, albeit, considerably smaller as compared to the $A^2\Pi$ state of the latter.

The present work is a highly accurate systematic study of the $X^2\Pi$ and $A^2\Sigma^+$ states of the ^{11}BNg diatomics, Ng = ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr, and ^{132}Xe through single reference coupled-cluster calculations [RCCSD(T)], extended correlation consistent basis sets, and complemented by a series of corrections some of them mandatory if we are after quantitative results. The essence of the B(^{2}P)−Ng "bonding" interaction is captured by the valence bond-Lewis (vbL) Schemes (1) and (2), clearly showing the cause of the expected weak van der Waals type interactions, taking into account as well the nature of the Ng atoms.

The BHe system obviously lacks π_p electrons which can be of some assistance to the van der Waals (vdW) interaction.

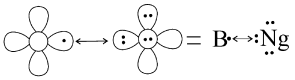
We have also examined at the coupled-cluster (CC) level the triatomics BNg$_2$ ($\tilde{X}^2B_1$), whose geometries and bonding can also be understood by inspecting the vbL diagram (1), but see below. Notice that, in essence, no experimental or theoretical results are available on BNg$_2$ complexes.

Scheme 1



B(^{2}P; M$_L$= ±1) Ng(^{1}S) $X^2\Pi$

Scheme 2



B(^{2}P; M$_L$= 0) Ng(^{1}S) $A^2\Sigma^+$

Table 1 presents all experimental and theoretical structural results on the BNg systems available in the literature concerning the $X^2\Pi$ and $A^2\Sigma^+$ states. It is worth noting the following: experimental results are scarce, limited to three dissociation energies (BNe,[5] BAr,[6] BKr[8]) and one bond distance for the $X^2\Pi_{1/2}$ state of BAr.[7] Theoretical predictions are also very limited, confined mostly to D_e and r_e for both $X^2\Pi$ and $A^2\Sigma^+$ states, three D_0 and one r_0 (BAr) values (see Table 1). Most importantly, the type of published calculations is not high enough, thus rendering the numbers of Table 1 of questionable validity, particularly for this kind of system; see the explicatory footnotes of Table 1. Therefore, the need for a comprehensive, high quality ab initio study of these very weakly interacting systems seems in order.

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Table 1. Experimental and Theoretical Results on ^{11}BNg, Ng = He, Ne, Ar, Kr, Xe, from the Literature[a]

state	species	D_e	D_0	r_e	r_0
			experiment		
$X^2\Pi_{1/2}$	BNe[b]		21.3 ± 0.2		
	BAr		102.4 ± 0.3[c]		3.606 ± 0.007[d]
	BKr[e]		159.4 ± 1.2		
			theory		
$X^2\Pi_{1/2}$	BNe[f]		17.5		
$X^2\Pi$	BAr[g]	94.7	75.1	3.671	3.703
	BAr	109.7[h]	106.1[I]	3.62[h]	
	BKr[h]	146.8		3.67	
	BXe[h]	196.8		3.73	
$A^2\Sigma^+$	BAr[g]	38.4		4.447	
	BAr[h]	45.2		4.43	
	BKr[h]	60.5		4.50	
	BXe[h]	67.8		4.70	

[a]Equilibrium distances are r_e and r_0 (Å), and dissociation energies are D_e and D_0 (cm^{-1}). [b]Ref 5. Laser Fluorescence Spectroscopy (LFS), under the assumption of barrierless dissociation to B($2s^12p^2$; ^{2}D). [c]Ref 6. LFS, under the assumption of barrierless dissociation. [d]Ref 7. LFS. [e]Ref 8. LFS; under the assumption of barrierless dissociation. [f]Ref 9. UCCSD(T)/aug-cc-pVQZ; after scaling (s = 1.25), D_0 = 20.0 cm^{-1}. [g]Ref 7. MRACPF/cc-pVQZ+spdfg diffuse functions. [h]Ref 10. UCCSD(T) /aug-cc-pVQZ/$_B$ ECP-Stuttgart/$_{Ng}$. [I]Ref 11. After applying an ad hoc scaling factor, s = 1.19, to the D_0 = 75.1 cm^{-1} (ref 7) also using the experimental D_0^0 = 102.4 cm^{-1} from ref 6.

For all BNg (Ng = He, Ne, Ar, Kr, and Xe) molecules, we report full potential energy curves (PEC), spectroscopic parameters, and permanent electric dipole moments. All our results for the $X^2\Pi$ states have been corrected for basis set superposition errors (BSSE), spin−orbit splittings (SO), core and scalar relativistic effects, and extrapolated to the complete basis set (CBS) limit. The BNg_2 triatomics have been treated at a lower level, but certainly our predicted numbers are judged to be quite reliable.

The paper is organized as follows. Section 2 refers to the computational details, section 3 (3A, 3B, and 3C) to results and discussion, whereas the closing section 4 is a short summary of this work.

2. BASIS SETS AND METHODS

Through all calculations, the augmented valence correlation consistent (cc) generally contracted basis sets have been used, namely aug-cc-pVnZ (= A$n\zeta$), where n = Q, 5, and 6 for both atoms B and Ng.[12−14] For the diatomics BHe, BNe, and BAr in particular, the A$n\zeta$ (n = Q, 5, and 6) basis sets have been employed, while for BKr, the A5ζ basis was used (A5ζ/$_B$ A5ζ/$_{Kr}$). For the very heavy Xe (Z = 54) atom, the inner 28 electrons ([Ar]$3d^{10}$) were replaced by the relativistic effective core potentials of Peterson et al.,[15] hereafter denoted as PP. The remaining 26 electrons are represented by the appropriate cc A5ζ basis set;[15] hence, the basis set of the BXe molecule can be written as A5ζ/$_B$ A5ζ-PP/$_{Xe}$(=A5ζ-PP).

As to the first four triatomics, BNg_2 (Ng = He−Kr) and BXe_2, the basis sets used are A5ζ/$_B$ A5ζ/$_{Ng}$ and A5ζ/$_B$ A5ζ-PP/$_{Xe}$, respectively.

For all BNg ($X^2\Pi$, $A^2\Sigma^+$) and BNg_2 ($\tilde{X}^2B_1$), Ng = He−Xe, the calculation approach followed is the single reference restricted coupled-cluster+singles+doubles+quasi-perturbative connected triples method, RCCSD(T).[16−18] Constraints of the C_{2v} Abelian point group have been imposed through all calculations.

Core corrections for the first three diatomics, $1s^2$ on B (BHe), $1s^2/1s^2$ (BNe), and $1s^2/2s^22p^6$ (BAr), have been taken

Table 2. Total Energies, E (E_h), Bond Lengths, r_e and r_0 (Å), Dissociation Energies, D_e and D_0 (cm^{-1}), Harmonic Frequencies, ω_e (cm^{-1}), and Anharmonic Corrections, $\omega_e x_e$ (cm^{-1}), Rotational Vibrational Coupling Constants, α_e (cm^{-1}), Dipole moments, μ_e (D), Equilibrium BSSE/r_e values (cm^{-1}), Separation Energies T (cm^{-1}) of the $X^2\Pi$ and $A^2\Sigma^+$ States of the BNg Species, Where Ng = He, Ne, Ar, Kr, Xe, Calculated at the RCCSD(T)/A$n\zeta$ Level of Theory. BSSE is Dynamically Corrected

BNg/n	$-E$	r_e	r_0	D_e	D_0[a]	ω_e	$\omega_e x_e$	$\alpha_e \times 10^2$	μ_e[b]	BSSE/r_e	T_e/T_0
					$X^2\Pi$						
BHe/5	27.504 803	3.551	4.617	16.6	3.33	26.6			0.010	0.52	0.0
BHe/6	27.505 272	3.540	4.587	17.2	3.48	27.4			0.010	0.15	0.0
BHe/CBS[c]		3.531	4.566	17.8	3.58						
BNe/5	153.461 55	3.520	3.808	36.5	21.9	28.8	6.0	3.9	0.022	5.17	0.0
BNe/6	153.465 95	3.506	3.793	37.8	22.8	29.6	6.1	3.8	0.022	1.98	0.0
BNe/CBS[c]		3.495	3.779	39.2	23.6						
BAr/5	551.685 55	3.585	3.692	119.5	97.1	46.6	4.1	1.4	0.080	11.2	0.0
BAr/6	551.690 12	3.577	3.682	122.6	99.9	47.2	4.1	1.4	0.080	4.82	0.0
BAr/CBS[c]		3.571	3.676	123.6	101.6						
BKr/5	2776.683 17	3.634	3.715	163.2	139.2	49.8	3.6	0.88	0.119	8.67	0.0
BKr/CBS[d]		3.611	3.690	170.4	146.0						
BXe/5-PP[e]	353.101 64	3.680	3.744	230.7	204.0	55.1	3.2	0.65	0.196	8.02	0.0
BXe/CBS[f]		3.664	3.728	238.0	210.9						
					$A^2\Sigma^+$						
BHe/6	27.505 214	4.648		4.47						0.03	12.7
BNe/6	153.465 84	4.337	4.928	14.1	6.15	16.0		4.5		0.98	23.7/16.6
BAr/6	551.689 78	4.382	4.580	50.0	36.9	29.2	5.1	0.96		2.38	72.6/63.0
BKr/5	2776.882 70	4.468	4.611	64.9	51.4	28.2	2.8			4.19	98.3/87.8
BXe/5-PP[e]	353.100 96	4.586	4.700	86.1	71.3	71.3	2.7	0.66		3.33	144.3/132.7

[a]$D_0 = D_e$ − ZPE. [b]Calculated through the finite field approach; field strengths = 10^{-4} a.u. [c]Complete basis set limit obtained at the RCCSD(T)/AQζ-A5ζ-A6ζ (Q56) level. [d](TQ5) Douglas−Kroll−Hess limit. [e]Effective core potential on Xe; see text. [f](TQ5)-PP CBS limit.

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into account by using the aug-cc-pCV5Z basis sets,[13,14] while no core corrections were applied to BKr and of course to BXe. Scalar relativistic corrections on BNg (Ng = He−Kr) were considered via the eighth-order Douglas-Kroll-Hess (DKH) approximation[19−21] in conjunction with the aug-cc-pVnZ-DK basis sets recontracted accordingly.[22]

Spin−orbit (SO) splittings were calculated by diagonalizing the $\hat{H}_e + \hat{H}_{SO}$ Hamiltonian within the valence internally contracted CASSCF+1+2 = MRCI/A6ζ (BHe, BNe, BAr), MRCI/A5ζ (BKr), and MRCI/A5ζ-PP (BXe) eigenvectors of $\hat{H}_e$; $\hat{H}_{SO}$ stands for the full Breit−Pauli operator. The CASSCF wave functions are obtained by distributing $5e^-$ to 5 orbitals for BHe ($2s2p/_B{+}1s/_{He}$) and 9 e^- to 7 orbitals ($2s2p/_B{+}np/_{Ng}$) for the rest of the BNg (Ng = Ne−Xe) species. Notice that the MRCI calculations have been employed solely for obtaining the SO splittings.

BSSE corrections, undoubtfully of importance for vdW molecules, were calculated through the usual counterpoise approach and along the entire B−Ng coordinate (dynamical BSSE[23−25]).

CBS limits for selected properties of the $X^2\Pi$ state of BNg (r_e, r_0, D_e, and D_0) have been estimated using the simple exponential

$$P_n = P_\infty + Ae^{-Bn}$$

and the mixed exponential-Gaussian

$$P_n = P_\infty + Ae^{-(n-1)} + Be^{-(n-1)^2}$$

formulas of Peterson and Dunning[26] and Peterson et al.,[27] respectively. In the formulas above P is a generic property, P_∞ its CBS limit, n is the cardinal number of the basis set, while A and B are fitting parameters. Our reported CBS limits are the arithmetic mean values of the above two relations.

Finally, the zero-point energy corrections (ZPE) and spectroscopic constants of the BNg diatomics were determined by numerically solving the radial Schrödinger equation for the B and Ng nuclei.

All calculations have been performed by MOLPRO2012.[28]

3. RESULTS AND DISCUSSION

Table 2 lists numerical results for both states ($X^2\Pi$ and $A^2\Sigma^+$) of the BNg (Ng = He−Xe) species. Notice that all values, but the total energies, have been corrected dynamically for BSSE. Table 3 refers to the SO interactions of the $X^2\Pi$ states and of the B atom calculated at the MRCI level, while Table 4 shows final results on the $X^2\Pi$ states of BNg after the imposition of SO, core, and scalar relativistic corrections. Core and relativistic corrections combined are indeed small, changing the bond distances and dissociation energies by δr_0 = +0.0016, +0.0068, −0.0033 Å and by δD_0 = −0.100, +0.23, +0.84 cm^{-1} for BHe, BNe, and BAr, respectively. Core corrections have not been applied to BKr and BXe, but only relativistic corrections through CBS TQ5-DKH (BKr) and TQ5-PP (BXe) limits. Final ω_e, $\omega_e x_e$, a_e, and μ_e constants of the $X^2\Pi$ state of BNg are those given in Table 2 at the RCCSD(T)/A6ζ level (Ng = He, Ne, and Ar) and RCCSD(T)/A5ζ, A5ζ-PP for Kr and Xe, respectively.

Table 3. Calculated and Experimental Spin-Orbit Splittings ΔT (cm^{-1}) = $^2\Pi_{3/2}$-$^2\Pi_{1/2}$ States of the BNg Molecules, Ng = He, Ne, Ar, Kr, and Xe and of the B Atom ($^2P_{3/2}$-$^2P_{1/2}$) at the MRCI Level Around Equilibrium

species	basis set	ΔT^a calcd.	ΔT exptl.
BHe	A6ζ	10.15	
BNe	A6ζ	10.53	
BAr	A6ζ	10.32	10.88 ± 0.08[b]
BKr	A5ζ	10.87	
BXe	A5ζ-PP[c]	15.35	
B	A6ζ	14.34	15.287[d]

[a]$\Delta T = A\Lambda\Sigma$, where A is the SO coupling constant. [b]Ref 29. [c]Effective core potentials. [d]Ref 4.

Table 4. Final (CBS, SO, Core, and Relativistically Corrected) Bond Lengths, r_0 (Å), and Dissociation Energies, D_0 (cm^{-1}), of the $X^2\Pi_{1/2,3/2}$ States of BNg, Where Ng = He, Ne, Ar, Kr, and Xe[a]

species[b]	r_0	$D_0(1/2-1/2)^c$	$D_0(3/2-3/2)^d$
BHe	4.568	−0.71	3.48
BNe	3.785	19.8 (21.3 ± 0.2)[e]	23.6
BAr	3.673 (3.606 ± 0.007)[e]	98.2 (102.4 ± 0.3)[e]	102.2
BKr	3.690	141.9 (159.4 ± 1.2)[e]	145.4
BXe	3.728	209.1	208.1

[a]Existing experimental values for easy comparison are in parentheses. [b]For details of obtaining the values above see the text. [c]$BNg(X^2\Pi_{1/2}) \rightarrow B(^2P_{1/2})+Ng(^1S)$. [d]$BNg(X^2\Pi_{3/2}) \rightarrow B(^2P_{3/2})+Ng(^1S)$. [e]See Table 1.

Table 5 lists numerical results for the triatomics BNg_2 (Ng = He−Xe) calculated at the RCCSD(T)/A5ζ level. Notice that only equilibrium BSSE corrections have been applied to all the BNg_2 triatomics.

Figure 1 illustrates the $X^2\Pi$ and $A^2\Sigma^+$ PECs of BNg (Ng = He−Xe) at the RCCSD(T)/A5ζ level dynamically corrected for BSSE.

A. BNg, $X^2\Pi$. The following deductions can be made from Tables 2, 3, and 4. (a) All B−Ng interaction energies D_0 are quite small as expected, the largest being about 210 cm^{-1} (BXe), clearly pointing to the van der Waals character of the BNg molecules; see also the vbL Scheme (1). Observe as well that with the exception of BHe, bond distances r_0 (BNg, Ng = Ne−Xe) remain more or less constant within ∼0.1 Å (see Table 4). Corresponding D_0 numbers of the $A^4\Sigma^-$ state of BNg are naturally much larger: 227, 92, 1908, 3467, and ∼6300 cm^{-1} for Ng = He, Ne, Ar, Kr, and Xe, respectively.[30] (b) The dissociation energies D_0 increase significantly from He (but see below) to Xe (see Table 4). As a matter of fact, they show excellent linear dependence as a function of the (experimental) static polarizabilities of Ng[31] (Figure 2). Extrapolating to the radioactive super heavy Ng radon (Rn; Z = 86, α = 5.3 $Å^3$), a good estimate of the D_0 of BRn is obtained, $D_0 \approx 280$ cm^{-1}. (c) Electric dipole moments increase monotonically from μ_e = 0.010 (BHe) to 0.196 D (BXe) (Table 2). The μ_e magnitude of BXe is about twice as large as the dipole moment of carbon monoxide, where μ_e (CO; $X^1\Sigma^+$) = 0.122 D.[32] It is quite interesting that the μ_e values display a perfect linear correlation with respect to the (experimental) polarizabilities α of the Ng atoms (Ng = He−Xe) with a slope of $d\mu/d\alpha$ = 0.048 D/$Å^3$. Thus, by extrapolating to the Rn atom as in (b), μ_e (BRn) ≈ 0.26 D. (d) It is of interest at this place to say a few words on the spin−orbit (SO) splittings of the BNg systems. Relative to the interaction energies D_0, the SO effect is significant for the lightest molecules (BHe and BNe), and then its relative contribution fades away (see Tables 3 and 4). The SO interaction in the $X^2\Pi$ state gives two $\Omega = \Lambda + \Sigma$ components,

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Table 5. Total Energies, E (E_h), Bond Lengths, r_{B-Ng} and r_{Ng-Ng} (Å), Angles, ∠NgBNg = θ (deg), Atomization Energies, AE_e and AE_0 (cm^{-1}), Harmonic Frequencies, $\omega_1(a_1)$, $\omega_2(a_1)$, and $\omega_3(b_2)$ (cm^{-1}), Dipole Moments, μ_e (D), and Equilibrium BSSE/r_e Values (cm^{-1}) of the $\tilde{X}^2B_1$ State of BNg_2, Where Ng = He, Ne, Ar, Kr, and Xe at the RCCSD(T)/A5ζ Level

Ng	$-E$	r_{B-Ng}	r_{Ng-Ng}	θ	$+AE_e$	$+AE_0$[a]	ω_1	ω_2	ω_3	μ_e	BSSE/r_e
He	30.408 117	3.5484	2.9711	49.5	42.1	−5.1	27.7	28.7	38.1		1.49
Ne	282.321 69	3.4872	3.3839	58.1	94.4	52.0	14.6	29.6	40.5	0.041	12.61
Ar	1078.770 00	3.5586	3.9892	68.2	321.6	263.4	18.9	42.1	55.3	0.132	29.29
Kr	5529.163 36	3.6056	4.2691	72.6	442.8	384.6	12.4	45.3	58.5	0.191	22.18
Xe	681.602 60	3.6879	4.4306	73.8	639.3	576.9	19.6	47.1	58.1	0.285	20.84

[a] $AE_0 = AE_e - 1/2\sum_{i=1}^{3}\omega_i$.

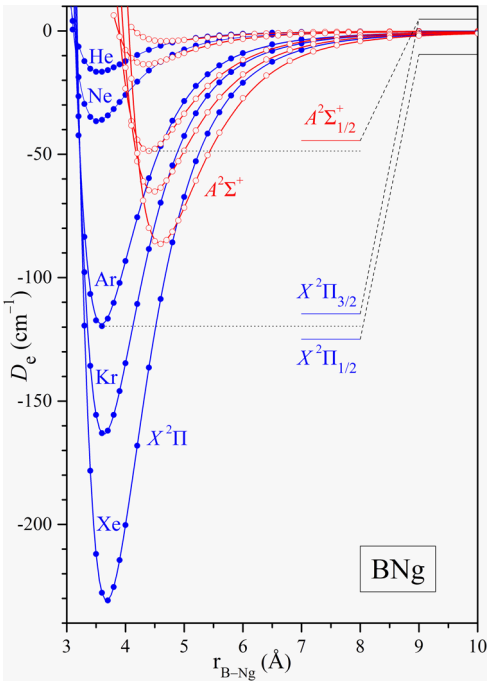

Figure 1. RCCSD(T)/A5ζ-BSSE corrected PEC's of the BNg diatomics, Ng = He−Xe. Blue ● and red ○ curves refer to the $X^2\Pi$ and $A^2\Sigma^+$ states. The shown SO splitting of BAr ($X^2\Pi_{3/2}$−$X^2\Pi_{1/2}$) and the B ($^2P_{3/2}$−$^2P_{1/2}$) + Ng (^1S) asymptote are 10.32 and 14.34 cm^{-1}, respectively.

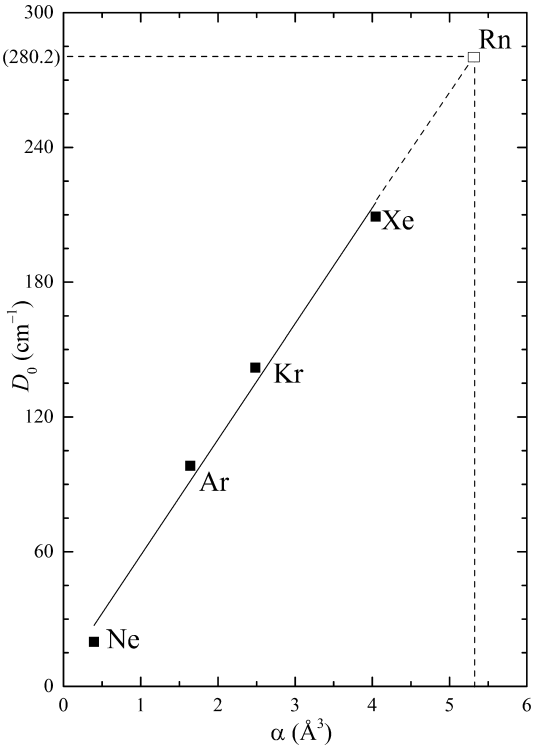

Figure 2. Extrapolation to Rn of the interaction energies D_0 of BNg ($X^2\Pi$), Ng = Ne−Xe versus the static experimental polarizabilities α of Ng.

1/2 and 3/2, the latter being the highest for all five BNg species (regular states). From Table 3, it can be seen that the 1/2−3/2 splitting (ΔT) of the BNg (Ng = He−Kr) is practically constant within 0.7 cm^{-1}; the splitting increases by ∼5 cm^{-1} in BXe. Notice as well the excellent agreement between experiment and theory in BAr, where ΔT = 10.88 ± 0.08[29] versus 10.32 cm^{-1}. Now taking into account the SO ΔT values of the BNg and that of the B atom, $\Delta T(^2P_{3/2} - {}^2P_{1/2})$ = 14.34 cm^{-1} (experimental value 15.287 cm^{-1}),[4] we obtain our final dissociation energies D_0 (see Table 4). The $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ states correlate to the $^2P_{1/2}$ and $^2P_{3/2}$ atomic states of the B atom, respectively; corresponding interaction energies are referred to as $D_0(1/2-1/2)$ and $D_0(3/2-3/2)$. Observe that with respect to the 1/2−1/2 components the BHe is unbound by 0.7 cm^{-1}, but it is bound by 3.5 cm^{-1} with respect to the 3/2−3/2 components. For the BNe molecule, the $D_0(3/2-3/2)$ is about 4 cm^{-1} larger than the $D_0(1/2-1/2)$ value (see Table 4). The percentage influence in the D_0 of the SO splittings diminishes drastically for the last three molecules BAr, BKr, and BXe. (e) A word is needed as to the accuracy of our parameters, as compared to the existing experimental values for the $X^2\Pi$ state. Assuming that the existing experimental values are correct, our largest discrepancy refers to the $D_0(1/2-1/2)$ value of BKr, 159.4 ± 1.2 vs 141.9 cm^{-1}, an error of about 10% (see Table 4). (f) Finally, the estimated number of vibrational levels of BNg are 1, 3, 5, 7, and 9 for Ng = He, Ne, Ar, Kr, and Xe, respectively.

B. BNg, $A^2\Sigma^+$. All our results on the $A^2\Sigma^+$ states of the BNg diatomics are collected in the second part of Table 2; Figure 1 displays the RCCSD(T)/A5ζ BSSE corrected PECs. We are reminded that no other than BSSE corrections have been applied to the $A^2\Sigma^+$ states. Our results, however, should be very reliable due to the smallness of core and scalar relativistic effects (vide supra). Notice also that no experimental results are available for this state, and also, there are no theoretical results for BHe and BNe. The quality of the limited theoretical values for the rest of the three species has been discussed in Introduction (see also Table 1).

We comment briefly on some general features of the $A^2\Sigma^+$ BNg states. In accordance with symmetry, the $A^2\Sigma^+$ states correlate to the $^2P_{3/2}$ component of the B(^2P; M_L = 0) + Ng(^1S) atoms (see Scheme 2). The SO splittings raise the $A^2\Sigma^+$

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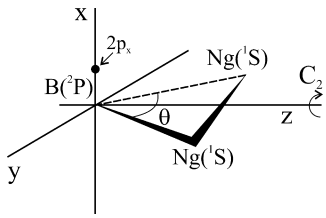
states of all BNg species by about 4.5 cm^{-1}, which is practically canceled due to the corresponding $^2P_{3/2}$-$^2P_{1/2}$ splitting of the B atom; the latter is ΔT = 14.34 cm^{-1} (Table 3), thus the $^2P_{3/2}$ component raises by $1/3\Delta T$ = 4.8 cm^{-1} above the line of the weighted average, thus $\Delta T(A^2\Sigma^+) - 1/3\Delta T(B) \approx 0$. We observe that (a) energy separations $T_0 = X^2\Pi - A^2\Sigma^+$, as expected, are quite small, ranging from 17 (BNe) to 133 cm^{-1} (BXe). (b) The BHe molecule is unbound; the 4.5 cm^{-1} well depth cannot sustain a single vibrational level. (c) Bond distances are by ∼1 Å larger and interaction energies (D_0) about 1/3 of the corresponding $X^2\Pi$ values (Tables 2 and 4). (d) The estimated number of vibrational levels of the BNg $A^2\Sigma^+$ states are 2, 4, 5, and 5 for Ng = Ne, Ar, Kr, and Xe, respectively. The morphology of the PECs (Figure 1) makes the $A^2\Sigma^+$-$X^2\Pi$ transitions problematic due to unfavorable Franck−Condon factors.

C. BNg_2, $\tilde{X}^2B_1$. All our numerical results on the symmetric triatomics BNg_2 (Ng = He−Xe) are given in Table 5 at the RCCSD(T)/A5ζ level. We list geometries, atomization energies (AE, AE_0) with respect to B (^2P) + 2Ng (^1S), harmonic frequencies, dipole moments, and basis set superposition errors at equilibrium ($BSSE/_{r_e}$). No other corrections have been considered other than the BSSEs which, incidentally, are significant, even at the A5ζ basis set level. No experimental data are available save certain observations on the existence of excited states of BNe_2[33] and BAr_2.[11,34] On the theoretical side (nonab initio) calculations predict AE_0 = 53.19 ± 0.3 and 295 ± 0.21 cm^{-1} for BNe_2[33] and BAr_2,[11,34] respectively.

The following conclusions can be drawn going through the numerical results of Table 5: (a) The BHe_2 complex although it presents a surface depth of 42 cm^{-1} (AE_e), it is unbound after including the harmonic ZPE correction. (b) All four BNg_2 complexes (Ng = Ne−Xe) are bent with the unique angle θ of the isosceles triangle NgBNg increasing monotonically from 58.1 (BNe_2) to 73.8 degrees (BXe_2). Scheme 3 below gives a

Scheme 3



perspective geometrical representation of the BNg_2 molecules, suggesting as well an interaction between the two Ng atoms [see conclusion (c)]. The symmetry-defining electron distribution on the B atom is perpendicular to the molecular plane. When θ = 60.0°, the isosceles triangle becomes equilateral as, practically, in the case of the BNe_2 molecule (θ = 58.1°). (c) The driving force of the acuteness of the angle θ, more generally, the bend structure of the BNg_2 species, seems to be the attractive interaction of the two Ng atoms. Indeed at equilibrium, the in situ Ng−Ng bond lengths (Table 5) are very close to the RCCSD(T)/A5ζ bond lengths of the free Ng_2 diatomics: 3.110, 3.787, 4.016, and 4.436 Å for Ne_2, Ar_2, Kr_2, and Xe_2, respectively. RCCSD(T)/A5ζ-BSSE corrected interaction energies D_0 of the free Ng_2 species are in relatively good agreement with the corresponding values given in ref 35 (experimental values in parentheses): 10.6 (16.3), 75.8 (84.8), 114.7 (126.6), and 163.5 (185.5) cm^{-1} for Ne_2, Ar_2, Kr_2, and Xe_2, respectively. Now the barrier-to-linearity (BtL), $BNg_2(\tilde{X}^2B_1;C_{2v}) \rightarrow NgBNg(^2\Pi_u;D_{\infty h})$ at the RCCSD(T)/A5ζ level including BSSE corrections, are BtL = 20.0, 75.9, 107.5, and 162.9 cm^{-1} for BNe_2, BAr_2, BKr_2, and BXe_2, respectively. The BtL numbers are smaller but very close to the interaction energies D_e = 25.8, 90.6, 125.8, and 173.0 cm^{-1} of the free Ng_2 diatomics, Ng = Ne, Ar, Kr, and Xe, respectively. The discussion above proves unequivocally that the BNg_2 complexes are absolutely floppy, their bent geometry being the result of the Ng−Ng in situ attractive interactions. From another perspective, the BNg_2 complexes can be thought as B(^{2}P) + $Ng_2(^1\sum_g^+)$ (see also Scheme 3). (d) In the light of the above, it is of no surprise that the atomization energies are in essence additive with respect to the BNg diatomics and the interactions of the free Ng_2 species at the same level of theory, that is, $AE_0 \approx 2xD_0(BNg; X^2\Pi) + D_0(Ng_2;^1\sum_g^+)$. For instance, in the BAr_2 case, we obtain [see Table 2 and conclusion (c) above], 2 × 97.1 + 75.8 = 270.0 cm^{-1} as contrasted to the calculated value of the BAr_2 (Table 5) AE_0 = 263.4 cm^{-1}. Finally, the same holds true for the dipole moments, being practically equal to the vector sum of the dipole moments ("bond moments") of the corresponding diatomic species, that is, $\mu_e(BNg_2;\tilde{X}^2B_1) = (2 \times [\mu_e(BNg;X^2\Pi]^2(1+\cos\theta))^{1/2}$. Indeed, through the vector sum we obtain [RCCSD(T) values in parentheses, Table 5], $\mu_e(BNg_2;\tilde{X}^2B_1)$ = 0.038 (0.041), 0.132 (0.132), 0.190 (0.191), and 0.313 (0.285) D for Ng = Ne, Ar, Kr, and Xe, respectively. Assuming a bond angle of $\theta \approx 75°$ for the BRn_2 complex (see the sequence of the θ angles in Table 5) and using the estimated dipole moment of BRn, $\mu_e \approx$ 0.26 D, we get μ_e (BRn_2) ≈ 0.4 D.

4. SUMMARY

We present the first systematic and high level ab initio study on the electronic structure of the $X^2\Pi$ and $A^2\Sigma^+$ states of the BNg van der Waals diatomics and the $\tilde{X}^2B_1$ C_{2v} triatomics BNg_2, Ng = He−Xe. With the exception of the spin−orbit interactions, which have been determined through the MRCI approach, the coupled-cluster single reference RCCSD(T) method was followed combined with quadruple to sextuple correlation consistent basis sets. For the $X^2\Pi$ states in particular, a series of corrections have been taken into account, namely (dynamical) BSSE, SO splittings, core, and scalar relativistic effects and CBS limits. We report energetics, spectroscopic parameters, interaction energies, and electric dipole moments. Good estimates of D_0 and μ_e values are also given for the $X^2\Pi$ state of the BRn system. Most of the results are reported for the first time, while the agreement with the existing experimental results is pretty good, considering the vdW nature of the BNg and BNg_2 complexes.

It is our belief that the comprehensiveness and the high calculational level of the present work resulting in practically definitive results, numerical or otherwise, will be useful to those interested in these van der Waals molecules.

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Notes

The authors declare no competing financial interest.

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