ELECTRON AFFINITIES OF BN, NO AND NF: COUPLED CLUSTER AND MULTIREFERENCE CONFIGURATION INTERACTION CALCULATIONS

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

The accurate adiabatic electron affinities (EA) of the BN, NO and NF molecules have been determined using the coupled cluster approach and multireference configuration interaction methods. By combining large doubly augmented correlation-consistent basis sets (through the sextuple zeta) and complete basis set extrapolations with corrections for core-valence correlation and relativistic effects, we find that the RCCSD(T) method gives EA(BN) = 3.153 eV in very close agreement with experiment and predicts EA(NF) = 0.247 eV. The RCCSD(T) and UCCSD(T) EA(NO) results, 0.008 and 0.031 eV, bracket the experimental value. For both the neutral and anionic ground state species the usual spectroscopic constants were derived.
Keywords: *Ab initio* calculations; RCCSD(T); UCCSD(T); Spectroscopic constants; Spin-orbit coupling; Electron affinity; Douglas–Kroll–Hess relativistic corrections; Complete basis set extrapolations.

In the previous paper[1] we investigated electronic ground state properties of NO and its ions using prevailingly the internally contracted multireference configuration interaction (icMRCI) method[2,3]. A major difficulty we met was associated with the estimation of the EA of NO. We return to the problem of calculating accurate EAs in this communication by offering a comparative study of the ground-state adiabatic EA of three nitrogen-containing diatomic molecules, NO, BN and NF, performed using the open-shell coupled cluster approach[4,5], icMRCI and multireference averaged coupled pair functions (MR-ACPF) methods[6] in conjunction with the series of doubly augmented correlation consistent basis sets.

The presently accepted EA value for NO is 0.026 ± 0.005 eV, as estimated by Travers et al.[7], who examined the photoelectron spectra of NO^- (and

O_2^-) using negative-ion photoelectron spectroscopy. Chen et al.[8] obtained by a least-square analysis of electron-capture detector experiments the adiabatic EA value for NO, EA(NO) = 0.8_5 ± 0.08 eV. For O_2, Chen et al.[8,9] proposed recently two values, EA(O_2) = 0.9 ± 0.05 and 1.07 ± 0.07 eV. However, the majority of experimental and theoretical EA(O_2) results of the other authors are ranging from 0.4 to 0.5 eV. When analyzing the ultraviolet photoelectron spectrum of O_2^- and determining EA of dioxygen, Lineberger and co-workers[10] have claimed that the large revision of EA(NO) [and EA(O_2)] proposed by Chen's interpretation would require very strong experimental evidence, which is not provided by the electron-capture detector experiments. Very good agreement of theoretical estimates of EA(NO) with experiment was achieved by Kalcher[11], McCarthy et al.[12], Stampfuß and Wenzel[13] and Boese et al.[14] Our own CASSCF/icMRCI calculations[1], making use of various active spaces and AO basis sets, predicted NO^- to be unstable with respect to NO.

The BN monomer, isolectronic with C_2, has a triplet ground state[15–17]. There are only a few spectroscopic studies on this species produced in a discharge or trapped in rare-gas matrices. A rough estimate of the EA has been proposed by Reid[18] using charge inversion spectrometry, EA(BN) = 2.9 ± 0.3 eV, being in good agreement with the *ab initio* value of Mawhinney et al.[19] (EA = 2.84 eV). Recently, Asmis et al.[20] applied the negative ion time-of-flight photoelectron spectroscopy to determine the EA, EA(BN) = 3.160 ± 0.005 eV, and selected spectroscopic constants for both the ground state of BN^- ($X^2\Sigma^+$) and the low-lying electronic states of the neutral.

The ground state of NF is of $^3\Sigma^-$ symmetry, as it is with the isoelectronic O_2. The spectroscopic constants of the NF $X^3\Sigma^-$ state have been determined by Jones et al.[21,22] from an analysis of the $b^1\Sigma^+$-$X^3\Sigma^-$ and $a^1\Delta$-$X^3\Sigma^-$ transitions. Highly correlated *ab initio* treatments of low-lying electronic states have been undertaken by Xantheas et al.[23] and Kardahakis et al.[24] to obtain the dissociation energy and spectroscopic constants. Czernek et al.[25] have calculated spectroscopic constants of both NF and its anion, and determined the dissociation energy, ionization energy and EA of NF using the correlation-consistent basis sets through the quadruple zeta.

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The doubly augmented correlation-consistent basis sets, d-aug-cc-pV*X*Z, *X* = 3–6 (refs[26–28]), have been mainly employed in calculations of both the anions and neutral parent molecules. Ground-state adiabatic electron affinities of BN, NO and NF were calculated using three methods: the partially

spin-restricted open-shell coupled cluster method including single, double and perturbative estimate of the connected triple excitations [RCCSD(T)] [4], the icMRCI [2,3] and the ACPF methods[6]. In the case of NO we have also used the spin-unrestricted coupled cluster [UCCSD(T)] approach[4,5]. The orbitals for the multireference treatments were obtained in complete-active-space SCF (CASSCF)[29] calculations. The full valence (2s2p) space consisted of 3σ–6σ, 1π, and 2π orbitals. In most calculations the core molecular orbitals were constrained to be doubly occupied in all electron configurations, but fully optimized. The multireference analog of the Davidson correction[30] was included for the approximate treatment of higher excitations (icMRCI+Q) on the potential energy functions (PEFs) and the pertinent spectroscopic constants. All the CASSCF, icMRCI, RCCSD(T), UCCSD(T) and ACPF calculations have been performed using the MOLPRO 2002 suite of programs[31].

To include the spin-orbit correction in the EA calculations, the spin-orbit constant A_v for NO was taken from experiment[32]. For the two other molecules, A_v was evaluated with the CI wave functions using the Breit–Pauli operator, as implemented in the MOLPRO code. Due to the limitation of this program, only the spdf orbital subset of the aug-cc-pV5Z basis set was employed in the icMRCI spin-orbit calculations. The usual spectroscopic constants of neutrals and anions have been derived numerically from the PEFs using the subroutine VIBROT, a component of the MOLCAS-4 suite of *ab initio* programs[33]. Vibration zero-point energy (ZPE) corrections to electron affinities, ZPE = $1/2\omega_e - 1/4\omega_e x_e$, were based either on experimental results, or on the RCCSD(T)/d-aug-cc-pV6Z values. The complete basis set (CBS) limits to E_e were calculated using the formula[34]

$$E(X) = E(\mathrm{CBS}) + A/X^3, \qquad (1)$$

where X is the cardinal number of the basis set. The CBS estimates for r_e and ω_e were calculated using an exponential function with three fitting parameters of the form[35,36]

$$P(X) = P(\mathrm{CBS}) + a \exp(-bX). \qquad (2)$$

The scalar relativistic contribution to EA was obtained from the Douglas–Kroll–Hess[37,38] quasirelativistic icMRCI/aug-cc-pV5Z calculations. To determine the CBS limit for EA, we have tested a number of formulas and finally used two kinds of extrapolations, according to Eq. (*2*) and the mixed exponential/Gaussian formula[39]

$$E^{EA}(X) = E^{EA}(CBS) + B \exp[-(X - 1)] + C \exp[-(X - 1)^2] \quad (3)$$

and the expression[34]

$$E^{EA}(X,Y) = [Y^3 E^{EA}(Y) - X^3 E^{EA}(X)]/[Y^3 - X^3], \quad (4)$$

where $Y = X - 1$. Equations (*3*) and (*4*) were used by, e.g., Musiał and Bartlett[40] for extrapolation of EAs of C_2 and O_3. As was mentioned earlier[34], inclusion of the DZ basis set in the fitting procedures lowers significantly the accuracy of an extrapolation and, therefore, we have not included the DZ results for the CBS estimates. At a given level of theory, the core-valence contributions may be obtained as the difference between the results obtained from all-electron and valence-electron correlated calculations[41]. In this study, core-valence correlation effects are evaluated at the R(U)CCSD(T) level using the augmented cc-pwCV5Z basis set of Peterson and Dunning[42].

RESULTS AND DISCUSSION

BN and BN⁻

The spectroscopic constants for the ground state of BN and its anion BN^- calculated by the RCCSD(T), icMRCI and MR-ACPF methods with the d-aug-cc-pV*X*Z basis sets are collected in Table I. For the neutral molecule, at the RCCSD(T)/d-aug-cc-pV6Z level, the calculated value of r_e, when corrected for zero-point vibration using B_e and α_e to give r_0 = 1.3313 Å, differs by only 0.0023 Å from the experimental r_0 value[16]. By analogy, the icMRCI method yields r_0 = 1.3325 Å. At the icMRCI/cc-pV5Z level, Peterson[43] obtained r_0 = 1.3328 Å, which is practically the same as our icMRCI/d-aug-cc-pV5Z result. The RCCSD(T) and icMRCI harmonic frequencies bracket the experimental value with the deviation about 3 cm^{-1}. The effect of basis set double augmentation on ω_e at the icMRCI/aug-cc-pV5Z level[43] is very small (0.8 cm^{-1}).

The icMRCI method yields the most accurate values of r_e and ω_e for BN^-; the CBS limits differ from experiment by 0.004 Å and 0.7 cm^{-1}, respectively. The d-aug-cc-pV*X*Z (*X* = Q, 5, 6) values of $r_e(BN^-)$ are in better agreement with experiment than that of Bruna and Grein[44], r_e = 1.2912 Å, obtained at the MRCI/6-311+G(2d) level. Anharmonicities $\omega_e x_e$ calculated by all mentioned methods also compare very well with experimental data for both the species. Inclusion of core-valence correlation effects decreases r_e by 0.005 Å,

TABLE I

Experimental and calculated spectroscopic constants for the ground electronic states of BN ($X^3\Pi$) and BN^- ($X^2\Sigma^+$) with the d-aug-cc-pV*X*Z (*X* = T, Q, 5, 6) basis sets. CBS extrapolations for E_e and r_e (ω_e) are calculated using Eqs (*1*) and (*2*), respectively

	Method	Basis set	E_e[a], E_h	r_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
BN	Experiment			r_0 = 1.329[b]	1519.2 ± 0.2[c]	12.6 ± 0.2[c]		
	RCCSD(T)	d-aug-cc-pVTZ	0.271604	1.3358	1499.2	14.1	1.533	0.0182
		d-aug-cc-pVQZ	0.288307	1.3292	1517.4	13.2	1.549	0.0181
		d-aug-cc-pV5Z	0.293244	1.3278	1520.7	13.1	1.551	0.0176
		d-aug-cc-pV6Z	0.294904	1.3274	1522.6	13.1	1.553	0.0180
		CBS	0.298937	1.3273	1522.5			
		aug-cc-pwCV5Z/VE[d]	0.293833	1.3276	1524.8			
		aug-cc-pwCV5Z/AE[e]	0.403138	1.3231	1537.5			
	icMRCI	d-aug-cc-pVTZ	0.265805	1.3371	1492.7	12.4	1.530	0.0172
		d-aug-cc-pVQZ	0.281575	1.3306	1511.9	12.5	1.545	0.0173
		d-aug-cc-pV5Z	0.286181	1.3292	1516.0	12.5	1.548	0.0173
		d-aug-cc-pV6Z	0.287723	1.3288	1517.4	12.2	1.549	0.0173
		CBS	0.291541	1.3287	1517.6			
	icMRCI + Q	d-aug-cc-pVTZ	0.274236	1.3387	1482.9	12.6	1.526	0.0174
		d-aug-cc-pVQZ	0.290555	1.3320	1503.0	12.7	1.542	0.0175
		d-aug-cc-pV5Z	0.295300	1.3306	1507.2	12.6	1.545	0.0175
		d-aug-cc-pV6Z	0.296887	1.3301	1508.6	12.4	1.546	0.0175
		CBS	0.300842	1.3301	1508.7			
	MR-ACPF	d-aug-cc-pVTZ	0.272456	1.3385	1484.7	12.5	1.527	0.0173
		d-aug-cc-pVQZ	0.288675	1.3318	1504.5	12.6	1.542	0.0175
		d-aug-cc-pV5Z	0.293397	1.3304	1508.7	12.6	1.545	0.0174
		d-aug-cc-pV6Z	0.294978	1.3299	1510.0	12.4	1.547	0.0175
		CBS	0.298907	1.3299	1510.2			

TABLE I
(*Continued*)

	Method	Basis set	E_e[a], E_h	r_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
BN^-	Experiment[f]			1.284 ± 0.005	1660 ± 40	12 ± 4		
	RCCSD(T)	d-aug-cc-pVTZ	0.384562	1.2949	1640.7	12.5	1.633	0.0176
		d-aug-cc-pVQZ	0.403022	1.2887	1660.1	13.0	1.649	0.0182
		d-aug-cc-pV5Z	0.408494	1.2874	1662.7	12.6	1.652	0.0181
		d-aug-cc-pV6Z	0.410358	1.2869	1666.5	12.9	1.653	0.0177
		CBS	0.414802	1.2869	1665.9			
		aug-cc-pwCV5Z/VE[d]	0.409067	1.2871	1660.7			
		aug-cc-pwCV5Z/AE[e]	0.519053	1.2830	1672.2			
	icMRCI	d-aug-cc-pVTZ	0.372000	1.2959	1637.2	11.6	1.628	0.0153
		d-aug-cc-pVQZ	0.389125	1.2898	1655.6	11.9	1.643	0.0154
		d-aug-cc-pV5Z	0.394144	1.2885	1659.2	11.9	1.647	0.0154
		d-aug-cc-pV6Z	0.395845	1.2880	1660.7	11.9	1.648	0.0154
		CBS	0.399980	1.2880	1660.7			
	icMRCI + Q	d-aug-cc-pVTZ	0.385632	1.2973	1629.2	11.6	1.624	0.0154
		d-aug-cc-pVQZ	0.403489	1.2910	1648.5	12.0	1.640	0.0155
		d-aug-cc-pV5Z	0.408686	1.2897	1652.4	12.0	1.644	0.0155
		d-aug-cc-pV6Z	0.410444	1.2892	1653.9	12.0	1.645	0.0155
		CBS	0.414762	1.2892	1654.0			
	MR-ACPF	d-aug-cc-pVTZ	0.383608	1.2972	1630.4	11.6	1.625	0.0154
		d-aug-cc-pVQZ	0.401374	1.2909	1649.5	11.9	1.640	0.0155
		d-aug-cc-pV5Z	0.406554	1.2895	1653.3	12.0	1.644	0.0155
		d-aug-cc-pV6Z	0.408308	1.2890	1654.9	12.0	1.645	0.0155
		CBS	0.412602	1.2889	1654.9			

[a] The total energy is reported as $-(E + 79)$. [b] Ref.[16] [c] Ref.[17] [d] Valence electrons correlated. [e] All electrons correlated. [f] Ref.[20]

and increases ω_e by 12 cm^{-1} for BN^- and the parent neutral molecule. For both species, the changes in r_e and ω_e with the cardinal number of the basis set are in accord with the general rule: In calculations at optimized geometry the bond distances shorten with increasing basis, resulting in a larger force constant and a higher vibrational frequency[45].

The electron affinities EA_e (the differences between the two minima on the ground state PEFs of the neutral molecule and its anion, without ZPE or other corrections) for the family of the d-aug-cc-pV*X*Z (*X* = 3–6) basis sets and four correlated methods are shown in Table II. The RCCSD(T) EA_e is

TABLE II

a) Electron affinities EA_e (in eV) of the BN molecule calculated using correlation-consistent basis sets

Basic set	RCCSD(T)	icMRCI	icMRCI + Q	MR-ACPF
d-aug-cc-pVTZ	3.07375	2.88971	3.03124	3.02460
d-aug-cc-pVQZ	3.12156	2.92659	3.07309	3.06670
d-aug-cc-pV5Z	3.13611	2.93782	3.08539	3.07916
d-aug-cc-pV6Z	3.14167	2.94215	3.09004	3.08387
CBS-1[a]	3.1437	2.9437	3.0916	3.0855
CBS-2[b]	3.1447	2.9445	3.0926	3.0865
CBS-3[c]	3.1493	2.9481	3.0964	3.0903

[a] Extrapolation using Eq. (*2*). [b] Extrapolation using Eq. (*3*). [c] Extrapolation using Eq. (*4*).

b) Corrections (in eV) to EA_e and final adiabatic EA(BN) values obtained by the RCCSD(T) method

Core correlation (RCCSD(T)/aug-cc-pwCV5Z)	0.01853
Vibrational correction	–0.00875
Spin-orbit correction	–0.00304
DK-scalar relativistic effects	–0.00286
Total correction to EA_e	0.00388
EA (CBS-1)	3.1476
EA (CBS-2)	3.1486
EA (CBS-3)	3.1532
Experiment[a]	3.160 ± 0.005

[a] Ref.[20]

closer to the experimental value than the multireference data. The MR-ACPF and icMRCI+Q values are comparable, and differ from the RCCSD(T) one by ≈0.06 eV. The most significant correction for the EA(BN) is the core correlation amounting to nearly 0.02 eV. The spin-orbit contribution to EA was taken as a spin-orbit splitting constant A_v for the $^3\Pi$ state of BN. Depending upon the extrapolation formula (Eqs (*2*)–(*4*)), we obtain the CBS limits for EA ranging from 3.148 to 3.153 eV at the RCCSD(T) level, in very good accord with experiment.

NO and NO⁻

Spectroscopic constants for the ground state of nitrogen oxide and its anion are shown in Table III. Due to convergency problems, we have used the aug-cc-pV*X*Z series for both species and coupled-cluster versions, while for the other methods we employed doubly augmented basis sets. For NO, both the open-shell coupled-cluster methods used (RCCSD(T) and UCCSD(T)) yield the most accurate values of r_e, which are larger by 0.0004 and 0.0007 Å, respectively, than the experimental value. Among the methods used, icMRCI reproduces best the NO experimental harmonic frequency and anharmonicity, with a deviation of 2.5 and 0.1 cm^{-1}, respectively.

For NO^- at the R(U)CCSD(T)/d-aug-cc-pV6Z level, reliable determination of spectroscopic constants could not be performed, because of convergence difficulties in calculating the PEF in a sufficiently wide range of interatomic distances. Therefore, the CBS limit for ω_e was calculated only from three points (T, Q, 5). Further, convergence problems outside the equilibrium distance region prevented us from using the ACPF approach to obtain the spectroscopic constants as well. However, there is also an uncertainty in the experimental data for the fundamental vibrational frequency. The values are ranging from ω_0 = 1284 ± 10 cm^{-1} (based on a vibrational photodetachment study of Maricq et al.[46]), through 1339 ± 80 cm^{-1} (ref.[47]) and 1363 cm^{-1} (determined from electron scattering experiments[48]), to ω_0 = 1470 ± 200 cm^{-1} (obtained by Siegel et al.[49] from an analysis of the photoelectron spectrum of NO^-). Jacox and Thompson[50] have tentatively assigned ω_0 of NO^- in a neon matrix equal to 1369.9 cm^{-1}. The icMRCI method yields a better fundamental frequency, $\omega_0 = \omega_e - 2\omega_e x_e$, and the interatomic distance than RCCSD(T). The icMRCI/CBS limit underestimates r_e by about 0.004 Å, and overestimates ω_0 by ≈8 cm^{-1}. The inclusion of the Davidson correction improves ω_e (and ω_0) and leads to a very good agreement with experiment. The UCCSD(T) and RCCSD(T) frequencies bracket

TABLE III

Experimental and calculated spectroscopic constants for the ground electronic states of NO ($X^2\Pi$) and NO^- ($X^3\Sigma^-$) with the (d-)aug-cc-pV*X*Z (*X* = T, Q, 5, 6) basis sets. CBS extrapolations for E_e and r_e (ω_e) are calculated using Eqs (*1*) and (*2*), respectively

	Method	Basis set	E_e[a], E_h	r_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
NO	Experiment[b]			1.15077	1904.20	14.075	1.67195	0.0171
	RCCSD(T)	d-aug-cc-pVTZ	0.725988	1.1565	1892.0	12.3	1.688	0.0171
		d-aug-cc-pVQZ	0.757922	1.1527	1909.3	12.1	1.700	0.0171
		d-aug-cc-pV5Z	0.768173	1.1517	1912.8	12.1	1.702	0.0171
		d-aug-cc-pV6Z	0.771764	1.1513	1915.5	12.2	1.703	0.0171
		CBS	0.779298	1.1512	1915.5			
		aug-cc-pwCV5Z/VE[c]	0.769618	1.1515	1915.5			
		aug-cc-pwCV5Z/AE[d]	0.888254	1.1491	1914.4			
	UCCSD(T)	d-aug-cc-pVTZ	0.726365	1.1569	1887.4	12.5	1.687	0.0173
		d-aug-cc-pVQZ	0.758313	1.1530	1904.7	12.4	1.699	0.0172
		d-aug-cc-pV5Z	0.768566	1.1521	1908.1	12.3	1.701	0.0172
		d-aug-cc-pV6Z	0.772156	1.1515	1908.9	12.1	1.702	0.0169
		CBS	0.779695	1.1515	1909.0			
	icMRCI	d-aug-cc-pVTZ	0.705508	1.1573	1882.4	14.0	1.685	0.0172
		d-aug-cc-pVQZ	0.734704	1.1536	1900.4	13.9	1.696	0.0171
		d-aug-cc-pV5Z	0.743953	1.1526	1904.3	14.0	1.699	0.0170
		d-aug-cc-pV6Z	0.747129	1.1522	1906.6	14.0	1.700	0.0170
		CBS	0.754064	1.1521	1906.7			
	icMRCI+Q	d-aug-cc-pVTZ	0.726416	1.1586	1872.7	14.0	1.682	0.0173
		d-aug-cc-pVQZ	0.756972	1.1548	1891.3	13.9	1.693	0.0171
		d-aug-cc-pV5Z	0.766593	1.1537	1895.3	13.9	1.695	0.0171
		d-aug-cc-pV6Z	0.769897	1.1535	1897.7	14.0	1.696	0.0171
		CBS	0.777163	1.1534	1897.8			
	MR-ACPF	d-aug-cc-pVTZ	0.724051	1.1584	1873.2	14.0	1.682	0.0173
		d-aug-cc-pVQZ	0.754502	1.1547	1891.6	13.9	1.693	0.0171
		d-aug-cc-pV5Z	0.764103	1.1536	1895.6	13.9	1.696	0.0171
		d-aug-cc-pV6Z	0.767403	1.1532	1897.9	14.0	1.697	0.0171
		CBS	0.774641	1.1531	1898.0			

TABLE III (*Continued*)

	Method	Basis set	E_e[a], E_h	r_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
NO^-	Experiment			1.271 ± 0.005[e]	ω_0 = 1369.9[f]	8[g]	1.427[g]	
	RCCSD(T)	d-aug-cc-pVTZ	0.724809	1.2694	1390.8	11.0	1.401	0.0149
		d-aug-cc-pVQZ	0.757059	1.2641	1405.3	10.8	1.413	0.0150
		d-aug-cc-pV5Z	0.767529	1.2629	1406.6	10.6	1.416	0.0150
		d-aug-cc-pV6Z	0.771247	1.2622				
		CBS	0.778817	1.2622	1407.6[h]			
		aug-cc-pwCV5Z/VE[c]	0.768936	1.2628				
		aug-cc-pwCV5Z/AE[d]	0.887548	1.2606				
	UCCSD(T)	d-aug-cc-pVTZ	0.725976	1.2713	1377.8	11.2	1.396	0.0152
		d-aug-cc-pVQZ	0.758249	1.2659	1392.3	11.0	1.408	0.0152
		d-aug-cc-pV5Z	0.768731	1.2647	1393.2	10.9	1.412	0.0152
		d-aug-cc-pV6Z	0.772451	1.2640				
		CBS	0.780026	1.2640	1394.1[h]			
	icMRCI	d-aug-cc-pVTZ	0.687815	1.2730	1378.8	11.3	1.393	0.0158
		d-aug-cc-pVQZ	0.716751	1.2680	1395.9	11.1	1.404	0.0160
		d-aug-cc-pV5Z	0.726019	1.2670	1399.3	11.1	1.406	0.0160
		d-aug-cc-pV6Z	0.729205	1.2666	1400.9	11.3	1.407	0.0158
		CBS	0.736062	1.2666	1400.9			
	icMRCI + Q	d-aug-cc-pVTZ	0.719962	1.2762	1362.6	11.3	1.386	0.0158
		d-aug-cc-pVQZ	0.750437	1.2711	1380.4	11.1	1.397	0.0160
		d-aug-cc-pV5Z	0.760101	1.2700	1384.0	11.0	1.400	0.0159
		d-aug-cc-pV6Z	0.763416	1.2695	1386.0	11.2	1.401	0.0158
		CBS	0.770655	1.2695	1386.0			
	MR-ACPF	d-aug-cc-pVTZ	0.718756	1.2726	–[i]	–	–	–
		d-aug-cc-pVQZ	0.749125	1.2683	–	–	–	–
		d-aug-cc-pV5Z	0.758769	1.2675	–	–	–	–
		d-aug-cc-pV6Z	0.762078	1.2671	–	–	–	–
		CBS	0.769289	1.2671	–	–	–	–

[a] The total energy is reported as –(E + 129). [b] Ref.[32]. [c] Valence electrons correlated. [d] All electrons correlated. [e] Ref.[7]. [f] Ref.[50]. [g] Ref.[32]. [h] The CBS limit calculated from three points (X = T, Q, 5). [i] Spectroscopic constants were not determined because of convergence difficulties in calculating the PEF in a sufficient interval of internuclear separations.

the icMRCI value. The core-valence correlation decreases r_e by about 0.002 Å for both NO and NO^-.

The electron affinities of NO with individual corrections are listed in Table IV. All three multireference methods fail to account for a positive value of EA(NO). This is in accord with a similar finding of Stampfuß and Wenzel[13] using the standard MRD-CI method. Although the enlargement of the active space within the CASSCF/icMRCI model and incorporation of

TABLE IV

a) Electron affinities EA_e (in meV) of the NO molecule calculated using correlation-consistent basis sets

Basic set	UCCSD(T)	RCCSD(T)	icMRCI	icMRCI + Q	MR-ACPF
d-aug-cc-pVTZ	–10.58	–32.08	–481.5	–175.6	–144.1
d-aug-cc-pVQZ	–1.74	–23.54	–488.5	–177.8	–146.3
d-aug-cc-pV5Z	4.49	–17.61	–488.0	–176.7	–145.2
d-aug-cc-pV6Z	8.03	–14.05	–487.7	–176.4	–144.9
CBS-1[a]	15.3	–6.8	–487.3[c]	–176.3[c]	–144.8[c]
CBS-2[b]	9.1 (10.1[c])	–13.1 (–12.0[c])	–487.5[c]	–176.2[c]	–144.7[c]
CBS-3[d]	12.9	–9.2	–487.3	–176.0	–144.5[c]

[a] Extrapolation using Eq. (*2*). [b] Extrapolation using Eq. (*3*). [c] Extrapolation includes only X = Q, 5 and 6 basis sets. [d] Extrapolation using Eq. (*4*).

b) Corrections (in meV) to EA_e and final adiabatic EA(NO) values obtained by the UCCSD(T) and RCCSD(T) methods

	UCCSD(T)	RCCSD(T)
Core correlation (aug-cc-pwCV5Z)	–0.4	–0.7
Vibrational correction	31.9	
Spin-orbit correction	–7.6	
DK-scalar relativistic effects	–6.3	
Total correction to EA_e	17.6	17.3
EA (CBS-1)	32.9	10.5
EA (CBS-2)	26.7 (27.7[a])	4.2 (5.3[a])
EA (CBS-3)	30.5	8.1
Experiment[b]	26 ± 5	

[a] Extrapolation includes only X = Q, 5 and 6 basis sets. [b] Ref.[7]

the Davidson correction improves the result, the EA still remains far from the experimental value[1]. Even an extrapolation of the active space to the full CI energy limit ($C(0)^2 = 1$, where $C(0)^2$ is the weight of the reference configuration in the icMRCI wave function) does not seem to lead to a physically correct result[1]. Of the correlated methods used, only UCCSD(T) yields the positive CBS limit 12.9 meV and the RCCSD(T) value lies by 22.1 meV lower. The spin-orbit correction to EA is taken as a half of the $^2\Pi_{3/2} - {}^2\Pi_{1/2}$ splitting in the $^2\Pi$ state of NO. As the vibrational correction is a dominant contribution, at the RCCSD(T) level of theory, NO^- becomes stable by virtue of zero-point energy. Depending on the extrapolation formula, RCCSD(T) predicts EAs from 4 to 11 meV, respectively, i.e., underestimating the measured value 26 ± 5 meV of Travers et al.[7] On the contrary, the UCCSD(T) values range from 27 to 33 meV in close agreement with the experimental value. Previously, Kalcher[11] determined an EA of 16 meV at the CCSD(T)/aug-cc-pV*X*Z/CBS (*X* = T, Q, 5) level including only spin-orbit (and ZPE) corrections. Somewhat larger CCSD(T) and QCISD(T)/aug-cc-pVTZ values were reported by McCarthy et al.[12] Stampfuß and Wenzel[13] have shown that the selective addition of the most important triple and quadruple excitations into the MRCI procedure[51], realized in the MRD-CI(TQ) method[13,52], yields EA(NO) = 15 meV. The W3 theory, which approximately accounts for post-CCSD(T) correlation effects, gives the value 29 meV [14].

NF and NF⁻

Calculated spectroscopic constants for both species at various levels of theory are summarized in Table V. For NF, the effect of switching to doubly augmented functions can be illustrated by comparing our r_e and ω_e values obtained using the d-aug-cc-pV6Z basis set with those obtained by Xantheas et al.[23] at the RCCSD(T)/cc-pV6Z level: the double augmentation leads to an increase in r_e of 0.0002 Å, and a decrease in ω_e of 1.6 cm^{-1}. The net effect of double augmentation decreases as the basis increases. The RCCSD(T)/CBS and icMRCI/CBS limits for r_e and ω_e are within the intervals of 0.0008 Å and 11 cm^{-1}, respectively, compared with experiment. Inclusion of core-valence correlation (using aug-cc-pwCV5Z basis set) leads to r_e that is by 0.002 Å smaller than the experimental value.

For NF^-, there are no experimental data. At the MR-ACPF level of theory, reliable spectroscopic constants could not be determined because of convergence difficulties hampered obtaining a sufficient part of the potential

TABLE V

Experimental and calculated spectroscopic constants for the ground electronic states of NF ($X^3\Sigma^-$) and NF^- ($X^2\Pi$) with the d-aug-cc-pV*X*Z (*X* = T, Q, 5, 6) basis sets. CBS extrapolations for E_e and r_e (ω_e) are calculated using Eqs (*1*) and (*2*), respectively

	Method	Basis set	E_e[a], E_h	r_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
NF	Experiment[b]			1.3169_8	1141.37	8.99	1.2057	0.0149
	RCCSD(T)[c]	cc-pV6Z	0.313766	1.3165	1152.7	8.6	1.206	0.0145
	RCCSD(T)	d-aug-cc-pVTZ	0.262019	1.3241	1132.9	8.2	1.192	0.0142
		d-aug-cc-pVQZ	0.298617	1.3188	1146.3	8.6	1.202	0.0143
		d-aug-cc-pV5Z	0.310853	1.3174	1150.0	8.6	1.205	0.0143
		d-aug-cc-pV6Z	0.315040	1.3167	1151.3	8.6	1.206	0.0145
		CBS	0.323650	1.3166	1151.7			
		aug-cc-pwCV5Z/VA[d]	0.312452	1.3173	1160.2			
		aug-cc-pwCV5Z/AE[e]	0.433643	1.3149	1153.6			
	icMRCI	d-aug-cc-pVTZ	0.234074	1.3236	1132.4	8.5	1.193	0.0142
		d-aug-cc-pVQZ	0.268137	1.3183	1146.1	8.8	1.203	0.0144
		d-aug-cc-pV5Z	0.279498	1.3169	1150.0	8.8	1.205	0.0144
		d-aug-cc-pV6Z	0.283368	1.3163	1151.8	8.8	1.206	0.0144
		CBS	0.291393	1.3162	1152.3			
	icMRCI + Q	d-aug-cc-pVTZ	0.258734	1.3274	1121.9	8.3	1.186	0.0142
		d-aug-cc-pVQZ	0.294391	1.3219	1136.0	8.6	1.196	0.0144
		d-aug-cc-pV5Z	0.306204	1.3205	1139.9	8.6	1.199	0.0144
		d-aug-cc-pV6Z	0.310231	1.3199	1141.8	8.7	1.200	0.0144
		CBS	0.318641	1.3198	1142.2			
	MR-ACPF	d-aug-cc-pVTZ	0.256407	1.3274	1121.2	8.4	1.186	0.0142
		d-aug-cc-pVQZ	0.291975	1.3220	1135.1	8.7	1.196	0.0144
		d-aug-cc-pV5Z	0.303776	1.3206	1139.0	8.7	1.198	0.0144
		d-aug-cc-pV6Z	0.307802	1.3200	1140.8	8.7	1.199	0.0144
		CBS	0.316187	1.3199	1141.2			

TABLE V
(*Continued*)

	Method	Basis set	E_e[a], E_h	r_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
NF^-	RCCSD(T)	d-aug-cc-pVTZ	0.267942	1.4948	748.5	6.1	0.936	0.0119
		d-aug-cc-pVQZ	0.305899	1.4897	751.6	6.0	0.942	0.0121
		d-aug-cc-pV5Z	0.318665	1.4881	754.3	6.0	0.944	0.0122
		d-aug-cc-pV6Z	0.323061	1.4875	755.6	6.2	0.945	0.0121
		CBS	0.331967	1.4873	759.4			
		aug-cc-pwCV5Z/VE[d]	0.320129	1.4895	756.8			
		aug-cc-pwCV5Z/AE[e]	0.441210	1.4868	758.6			
	icMRCI	d-aug-cc-pVTZ	0.222486	1.4988	765.9	5.8	0.931	0.0118
		d-aug-cc-pVQZ	0.257377	1.4934	768.8	5.7	0.938	0.0120
		d-aug-cc-pV5Z	0.269101	1.4917	771.4	5.7	0.940	0.0120
		d-aug-cc-pV6Z	0.273137	1.4909	771.8	5.6	0.941	0.0120
		CBS	0.281326	1.4906	773.4			
	icMRCI + Q	d-aug-cc-pVTZ	0.258466	1.5045	751.3	6.0	0.924	0.0121
		d-aug-cc-pVQZ	0.295211	1.4990	754.7	5.8	0.931	0.0122
		d-aug-cc-pV5Z	0.307428	1.4972	757.6	5.8	0.933	0.0122
		d-aug-cc-pV6Z	0.311628	1.4964	758.0	5.7	0.934	0.0122
		CBS	0.320273	1.4961	759.6			
	MR-ACPF	d-aug-cc-pVTZ	0.259102	1.4897				
		d-aug-cc-pVQZ	0.295590	1.4873				
		d-aug-cc-pV5Z	0.307747	1.4863				
		d-aug-cc-pV6Z	0.311932	1.4859				
		CBS	0.320510	1.4856				

[a] The total energy is reported as $-(E + 154)$. [b] Refs[21,22] [c] Ref.[23] [d] Valence electrons correlated. [e] All electrons correlated.

energy curve. As seen from Table V, the RCCSD(T)/CBS limit for r_e lies between the values calculated using the icMRCI and MR-ACPF methods. The RCCSD(T)/CBS and icMRCI+Q/CBS limits for the harmonic frequency are very similar, being about 14 cm^{-1} lower than that for icMRCI. Core-valence correlation effects practically do not change ω_e.

The EAs for NF calculated by four correlated methods are listed in Table VI. While the RCCSD(T) approach yields positive values, the icMRCI method gives negative ones, the sign of which is reversed again by applying the Davidson correction. The MR-ACPF EAs lie between the RCCSD(T) and

TABLE VI

a) Electron affinities EA_e (in eV) of the NF molecule calculated using correlation-consistent basis sets

Basic set	RCCSD(T)	icMRCI	icMRCI + Q	MR-ACPF
d-aug-cc-pVTZ	0.16117	–0.31533	–0.00729	0.07333
d-aug-cc-pVQZ	0.19815	–0.29279	0.02231	0.09837
d-aug-cc-pV5Z	0.21258	–0.28292	0.03331	0.10806
d-aug-cc-pV6Z	0.21826	–0.27840	0.03801	0.11238
CBS-1[a]	0.2219	–0.2749	0.0406	0.1150
CBS-2[b]	0.2213	–0.2765	0.0402	0.1143
CBS-3[c]	0.2261	–0.2722	0.0445	0.1183

[a] Extrapolation using Eq. (*2*). [b] Extrapolation using Eq. (*3*). [c] Extrapolation using Eq. (*4*).

b) Corrections (in eV) to EA_e and final adiabatic EA(NF) values obtained by the RCCSD(T) method

Core correlation (RCCSD(T)/aug-cc-pwCV5Z)	–0.00299
Vibrational correction	0.02383
Spin-orbit correction	0.00529
DK-scalar relativistic effects	–0.00494
Total correction to EA_e	0.02119
EA (CBS-1)	0.2431
EA (CBS-2)	0.2425
EA (CBS-3)	0.2473

icMRCI results. In context with this discrepancy between the RCCSD(T) and multireference results it is worth mentioning that the active space expansion by an additional σ orbital, i.e. leading to the (3σ–7σ,1π,2π) AS, does not alter significantly the MR results. Particularly at the d-aug-cc-pV6Z basis set level, all three MR approaches yield values by about 0.024 eV larger compared with those listed in Table VI, i.e. somewhat closer to the RCCSD(T) values. It should be noted that EA_e obtained at the RCCSD(T)/aug-cc-pwCX5Z/AE level of theory is by ≈0.02 eV lower than the RCCSD(T)/CBS one. The various CBS limits for EA_e (within a given *ab initio* method) differ only slightly. The vibrational correction is a dominant (and positive) contribution. The spin-orbit correction for NF^- ($X^2\Pi$) was calculated and taken, similarly to NO($X^2\Pi$), as a half of the spin-orbit splitting constant. In response to the remarks of Nicklass et al.[53] that accurate spin-orbit coupling calculations of the halogen atoms require the addition of a very tight p function to the cc-pCV*X*Z basis sets, we examined the quality of the icMRCI/aug-cc-pV5Z calculation (with the state-averaged 2s2p+3s3p3d active space) for the spin-orbit splitting of the F atom. The corresponding deviation in using the spdf subsets of the aug-cc-pV5Z and (aug-cc-pCV5Z+p_{tight}) basis sets is very small (396.7 vs 397.7 cm^{-1}), justifying the use of our basis set in the spin-orbit calculations of NF^-.

Our final estimate, EA(NF) = 0.247 eV, obtained by the RCCSD(T) method, is significantly larger than that previously reported by Czernek et al.[25] (EA(NF) = 0.029 eV) using the CCSD(T)/cc-pwC*X*Z (*X* = D, T, Q) model.

CONCLUSIONS

Spectroscopic constants of three ground-state anions BN^-, NO^-, NF^- and the parent neutral molecules, as well as the adiabatic electron affinities of BN, NO and NF were calculated using the R(U)CCSD(T), icMRCI(+Q) and MR-ACPF methods in conjunction with the (d)-aug-cc-pV*X*Z basis sets, *X* = 3–6. For the $BN^-(X^2\Sigma^+)$ and $NO^-(X^3\Sigma^-)$ anions, the RCCSD(T) and icMRCI treatments yield the bond distances as well as the harmonic frequencies of comparable quality. In calculating accurate EAs, we have used three extrapolation formulas for the CBS limits and included the ZPE, core-valence, spin-orbit and Douglas–Kroll relativistic corrections. For NO, the UCCSD(T) method yields an EA of 0.031 eV within experimental error, while the RCCSD(T) method underestimates the measured value by about 0.018 eV. The EA for BN determined at the RCCSD(T) level, 3.153 eV, compares very well with experiment; for NF the RCCSD(T) method predicts EA = 0.247 eV.

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