Theoretical Investigation of the Ground X³Σ⁻ State of Nitrogen Bromide

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The spectroscopic constants and the dissociation energy of the ground X³Σ⁻ state of NBr have been computed using correlated wave functions and correlation-consistent orbital basis sets up to quintuple ζ quality. Our best estimates for the equilibrium separation (r_e) is 1.780 Å and for the dissociation energy (D_e) 49.5 kcal/mol, suggesting that previous estimates obtained from indirect experimental measurements are in error by as much as 15 kcal/mol. The spectroscopic constants computed at the RCCSD(T)/aug-cc-pV5Z level of theory are $\omega_e = 694.5$ cm⁻¹, $\omega_e\chi_e = 4.14$ cm⁻¹, and $\alpha_e = 0.0039$ cm⁻¹. The linear variation of D_e for the NX species (X = F, Cl, Br) supports a prediction of about 35 kcal/mol for the dissociation energy of NI.

Introduction

Continuing our studies on nitrogen monohalides,[1−3] we present here ab initio results on the electronic properties of the ground X³Σ⁻ state of nitrogen bromide (NBr). Monohalides of the group VA(15) elements are of practical interest since, being isovalent with O_2, they are potential candidates for chemical energy storage systems.[4]

NBr was first observed by Elliot[5] almost 60 years ago, who hypothesized a transition between two (unknown at that time) states of NBr after admitting bromine into a stream of active nitrogen. Since then quite a few experimental studies have appeared in the literature,[6] but we are aware of only one experimental paper[7] referring to the spectroscopic constants r_e, ω_e, $\omega_e\chi_e$, α_e, as well as the dissociation energy D_e of the ground X³Σ⁻ state of NBr. These researchers[7] have obtained a $D_e = 67 \pm 5$ kcal/mol from the highest v' value observed in the emission b¹Σ⁺ → X³Σ⁻ from the process N(⁴S) + Br(²P₃/₂) → NBr* → NBr + $h\nu$ using a Birge−Sponer extrapolation scheme. Our calculations suggest (vide infra) that this D_e value is overestimated by as much as 15 kcal/mol, mainly due to the use of the Birge−Sponer extrapolation method.[8]

To the best of our knowledge no previous ab initio calculations have appeared in the literature for the dissociation energy and/or spectroscopic constants of NBr prior to our study.

Computational Approach

To obtain an accurate D_e value for the process N(⁴S) + Br(²P₃/₂) → NBr(X³Σ⁻), we have performed ab initio calculations using (i) complete active space self-consistent field (CASSCF), (ii) multi reference configuration interaction (MRCI) based on CASSCF + single + double excitations (CASSCF + 1 + 2), and (iii) coupled cluster plus single and double excitations with a perturbative estimate of the triple excitations from a restricted Hartree−Fock (RHF) reference wave function [RCCSD(T)] methods. The CASSCF reference function was constructed by allotting the 12 "valence" (active) electrons of NBr to the eight valence functions of the system, i.e., (core)³⁰-

TABLE 1: SCF and CISD Energies *E* (Hartree) of the Atoms N(⁴S) and Br(²P) in a Series of cc-Basis Sets

basis sets	N(⁴S)		Br(²P)	
	$-E_{SCF}$	$-E_{CISD}$	$-E_{SCF}$	$-E_{CISD}$
cc-pVDZ	54.388414	54.477042	2572.36491	2572.47166
aug-cc-pVDZ	54.389871	54.484639	2572.36719	2572.48006
cc-pVTZ	54.397358	54.510958	2572.44021	2572.59215
aug-cc-pVTZ	54.397610	54.512798	2572.44047	2572.59505
cc-pVQZ	54.400176	54.520406	2572.44296	2572.60937
aug-cc-pVQZ	54.400225	54.520979	2572.44297	2572.61045
cc-pV5Z	54.400853	54.523306	2572.44324	2572.61462
aug-cc-pV5Z	54.400856	54.523543	2572.44325	2572.61517
numerical HF[a]	54.400934		2572.441333	

[a] Numerical Hartree−Fock, ref 15.

[(4s4p)$_{Br}$; (2s2p)$_N$].[12] This results in a wave function comprised of 96 configuration state functions (CSFs) with an asymptotic description of the N(⁴S) + Br(²P) fragments exactly at the SCF level. At this stage, care has been taken for the wave function to obey symmetry and equivalence restrictions,[9] that is Λ = |M| = 0. Dynamical valence correlation was extracted within the internally contracted MRCI scheme[10] by allowing single and double excitations out of the CASSCF reference (icMRCI). Our highest level of calculation can be considered the icMRCI+Q (icMRCI plus the multireference analogue of the Davidson correction[11]) as well as the RCCSD(T) methods.

The basis sets employed are the correlation-consistent sets cc-pVxZ and aug-cc-pVxZ of Dunning and co-workers[12] with x = D, T, Q, and 5. The quality of the cc-basis sets and their ability to successfully describe a variety of molecular properties are well-established by now.[13] Our largest expansion, aug-cc-pV5Z, contains 267 generalized contracted spherical Gaussian functions.

For the X³Σ⁻ state of NBr and for all basis sets employed, we report total energies, full potential-energy curves, spectroscopic constants (D_e, r_e, ω_e, $\omega_e\chi_e$, α_e), and dipole moments (μ). The spectroscopic constants were extracted using a Dunham analysis by fitting 20 energy points around equilibrium, spanning

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TABLE 2: Results on the Ground $X^3\Sigma^-$ State of $^{14}N^{79}Br^a$

method	basis set	−E	r_e	D_e	ω_e	$\omega_e\chi_e$	α_e	μ
CASSCF	cc-pVDZ	2626.79448	1.888	25.8	549.1	5.39	0.0046	
	cc-pVTZ	2626.88553	1.854	30.1	588.9	5.18	0.0044	
	cc-pVQZ	2626.89187	1.849	30.6	591.5	5.11	0.0044	
	cc-pV5Z	2626.89303	1.848	30.7	593.9	5.21	0.0043	
	aug-cc-pVDZ	2626.80208	1.873	28.3	575.3	5.27	0.0044	
	aug-cc-pVTZ	2626.88656	1.852	30.4	590.4	5.12	0.0044	
	aug-cc-pVQZ	2626.89212	1.848	30.7	590.8	5.30	0.0046	
	aug-cc-pV5Z	2626.89315	1.848	30.8	592.5	5.16	0.0044	
icMRCI	cc-pVDZ	2626.99823	1.852	35.4	601.7	4.88	0.0043	0.908
	cc-pVTZ	2627.16210	1.805	44.1	659.3	4.66	0.0041	1.106
	cc-pVQZ	2627.19236	1.795	47.1	669.0	4.48	0.0041	1.107
	cc-pV5Z	2627.20217	1.791	48.3	674.8	4.53	0.0041	1.067
	CBS-limit		1.791	48.5				
	aug-cc-pVDZ	2627.02031	1.838	40.2	627.3	4.63	0.0041	0.961
	aug-cc-pVTZ	2627.16941	1.801	46.0	663.0	4.59	0.0041	1.084
	aug-cc-pVQZ	2627.19532	1.794	48.0	671.0	4.46	0.0041	1.065
	aug-cc-pV5Z	2627.20356	1.791	48.7	675.2	4.48	0.0040	1.088
	CBS-limit		1.791	48.8				
icMRCI+Q	cc-pVDZ	2627.0143	1.848	36.7	607.6	4.82	0.0042	
	cc-pVTZ	2627.1888	1.801	46.1	666.0	4.59	0.0041	
	cc-pVQZ	2627.2222	1.791	49.5	677.0	4.40	0.0040	
	cc-pV5Z	2627.2329	1.786	50.9	683.1	4.48	0.0041	
	CBS-limit		1.786	51.3				
	aug-cc-pVDZ	2627.0402	1.834	41.9	633.0	4.54	0.0040	
	aug-cc-pVTZ	2627.1976	1.797	48.4	670.9	4.51	0.0041	
	aug-cc-pVQZ	2627.2257	1.790	50.6	678.6	4.21	0.0040	
	aug-cc-pV5Z	2627.2345	1.786	51.4	683.4	4.41	0.0040	
	CBS-limit		1.786	51.5				
RCCSD(T)	cc-pVDZ	2627.01166	1.841	36.1	625.8	4.41	0.0040	
	cc-pVTZ	2627.19039	1.797	46.3	679.2	4.25	0.0039	
	cc-pVQZ	2627.22540	1.787	49.8	688.3	4.12	0.0039	
	cc-pV5Z	2627.23682	1.783	51.4	693.7	4.15	0.0039	
	CBS-limit		1.783	51.8				
	aug-cc-pVDZ	2627.03877	1.828	41.7	649.7	4.21	0.0038	
	aug-cc-pVTZ	2627.20003	1.793	48.7	683.4	4.24	0.0039	
	aug-cc-pVQZ	2627.22925	1.786	51.0	690.5	4.12	0.0039	
	aug-cc-pV5Z	2627.23851	1.783	51.9	694.5	4.14	0.0039	
	CBS-limit		1.783	52.0				
exp^b			1.79	67 ± 5	691.8	4.72	0.0040	

^{a} Absolute energies E (Hartree), equilibrium bond lengths r_e (Å), dissociation energies D_e (kcal/mol), spectroscopic constants ω_e (cm^{-1}), $\omega_e\chi_e$ (cm^{-1}), α_e (cm^{-1}), and dipole moments μ (D) in different methodologies and basis sets. ^{b} Reference 7.
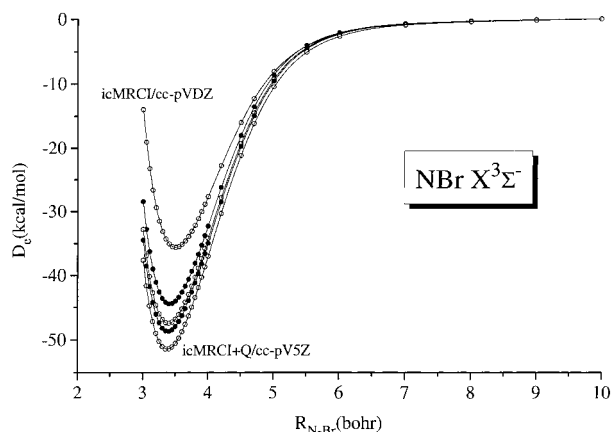

Figure 1. icMRCI potential-energy curves with the cc-pVDZ to cc-pV5Z basis sets; the lowest PEC is at the icMRCI+Q/cc-pV5Z level.

a distance of 3.0−4.2 bohr. By exploiting the convergence properties of the cc-basis sets, we also report the complete basis set limit (CBS) of the D_e and r_e parameters. All calculations were performed using the MOLPRO suite of programs.[14]

Results and Discussion

The SCF and CISD energies of N(^{4}S) and Br(^{2}P) atoms are shown in Table 1. We note that the SCF energy of N with the aug-cc-pV5Z set is just 0.08 mhartree above the numerical HF number,[15] while the corresponding value for the Br atom is *lower* than the numerical HF result by 1.9 mhartree. This obvious discrepancy in the Br atom is due to a symmetry breaking effect[16] caused by the C_{2v} symmetry restrictions imposed on the SCF calculations. By performing an ensemble (over the three $M_L = 0, \pm1$ components) SCF calculation with the aug-cc-pV5Z set, we obtain an upper bound to the numerical HF value by 0.06 mhartree. We report here the $M_L = 0$ (A$_1$) SCF energy results for the Br atom since the CASSCF wave function of NBr correlates at infinity to the $M_L = 0$ projection of the Br atom.

Figure 1 shows PECs at the icMRCI level of theory in the cc-pVDZ through cc-pV5Z basis sets, referring to the process
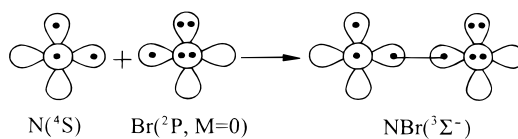
The equilibrium CAS-atomic populations (cc-pV5Z basis) clearly show that the two atoms are held together by a pure σ-bond, with a transfer of 0.12 e$^-$ from Br to N:

$$4s^{1.96}4p_z^{1.05}4p_x^{1.89}4p_y^{1.89}(dfg)^{0.10}/2s^{1.89}2p_z^{1.07}2p_x^{1.06}2p_y^{1.06}(dfg)^{0.05}$$

Table 2 summarizes all our pertinent numerical results. It is interesting to point out that at the SCF level (not listed), the binding energy ranges from −2.6 (cc-pVDZ) to +3.3 (cc-pV5Z) kcal/mol. This means that the binding energy is essentially correlation energy, of course defining the correlation energy with respect to a single reference. Imposing the requirement of a minimum space size consistent (CASSCF) wave function, a D_e of ∼31 kcal/mol is obtained, a value about 60% of the corresponding MRCI+Q result. It is also of interest to mention that the size nonextensivity of the MRCI function increases from 6.87 (cc-pVDZ) to 12.72 mhartree (cc-pV5Z), with corresponding numbers of 0.83−2.47 mhartree at the MRCI+Q level.

Table 2 reveals that the double-ζ quality basis set is inadequate in describing any property of the system, while the triple-ζ quality set is the absolute minimum for obtaining semiquantitative results. At least basis sets of quadruple-ζ quality are required in order to obtain quantitative results; the results are converged with the 5Z set. This is also obvious from the CBS limits reported in Table 2 for the D_e and r_e values. The CBS-limits for the plain and augmented sets were obtained using the exponential function[17,13]

$$P_x = P_{CBS} + A \exp(-Bx)$$

where x is the cardinal number of the basis set (2−5 for double through quintuple) and A and B are adjustable parameters.

At the highest level of calculation, RCCSD(T)/aug-cc-pV5Z, a value of D_e = 51.9 kcal/mol is obtained, slightly different from the icMRCI+Q/aug-cc-pV5Z result of 51.4 kcal/mol (cf. Table 2). These numbers are only 0.1 kcal/mol away (smaller) from the corresponding CBS limits obtained using the exponential extrapolation. The difference of 3.2 kcal/mol in the CBS limits of D_e with the RCCSD(T) and icMRCI/aug-cc-pV5Z methods is significant and can probably be attributed to the size nonextensivity of the MRCI approach as well as to the error in the internal contraction scheme. The latter effect has been previously estimated to reduce D_e by 2.0 kcal/mol for NCl[1,3] and by a comparable amount[18] for O_2 and F_2. To compare our best estimate for D_e with the one that can be measured experimentally, a correction is required for the spin−orbit coupling of the Br atom, which causes a significant splitting of its ^2P state. The "true" (experimental) binding energy can be approximated by the formula

$$D_e^{exp} = D_e - \tfrac{1}{3}\Delta E(^2P_{3/2} - {}^2P_{1/2})_{Br} +$$
$$\tfrac{1}{2}\Delta E(^3\Sigma_{\pm1}^- - {}^3\Sigma_0^-)_{NBr} \quad (1)$$

where $\Delta E(^3\Sigma_{\pm1}^- - {}^3\Sigma_0^-)_{NBr}$ is the zero-field splitting of the NBr molecule. Taking this last splitting as zero (the maximum value is no more[6] than 25 cm^{-1}) and $\Delta E(^2P_{3/2} - {}^2P_{1/2})_{Br} = 3685$ cm^{-1} = 10.54 kcal/mol,[19] we obtain D_e^{exp} = 52.0−3.51 = 48.5 kcal/mol. Assuming that core-valence correlation amounts to no more than[3] 1 kcal/mol, we finally obtain a value of D_e = 49.5 kcal/mol.

A comparison with the dissociation energies[3] of the isovalent monohalides NF and NCl is in order. For these species, the reported D_e values[3] without spin−orbit corrections are 76.6 (NF) and 64.6 (NCl) kcal/mol. Correcting as before for the spin−orbit splittings of F and Cl (404 and 881 cm^{-1}, respectively[19]) according to eq 1, we obtain D_e^{exp}(NF) = 76.2 kcal/mol and D_e^{exp}(NCl) = 63.8 kcal/mol. A crude estimate for nitrogen iodide (NI) can be obtained from the incremental drop in the RCCSD(T)/CBS D_e values (uncorrected with respect to the spin−orbit splittings) of NX, X = F, Cl, and Br assuming that

this trend continues for NI. A constant incremental decrease of ∼12 kcal/mol in D_e is observed from NF to NBr; therefore, a value of 40 kcal/mol can be suggested for NI. Correcting this value for the spin−orbit splitting of the ^2P state of the I atom (7603 cm^{-1}), we obtain D_e^{exp}(NI) ≈ 33 kcal/mol. A similar D_e value for NI is obtained by using the experimental ω_e = 590 cm^{-1} [20] in conjunction with Badger's rule[21] for obtaining an estimate of r_e(NI) = 2.0 Å. From the icMRCI+Q/cc-pV5Z PEC of NBr at this interatomic distance, a D_e value of 43 kcal/mol is extracted, which upon correction for the iodine spin−orbit splitting gives D_e ≈ 36 kcal/mol. Therefore, a mean D_e value of 35 kcal/mol can be finally suggested for the NI molecule.

Regarding the spectroscopic constatnts, we obtain r_e = 1.783 Å at the RCCSD(T)/(aug)-cc-pV5Z level and 1.786 Å at the icMRCI+Q/(aug)-cc-pV5Z level. Core-valence effects are expected to decrease[22,3] the equilibrium bond length by 0.002−0.003 Å, therefore yielding a best estimate of 1.780 Å. This r_e value as well as the other spectroscopic constants (ω_e, $\omega_e\chi_e$, α_e) are in very good agreement with the experimental results[7] (cf. Table 2), although the latter were "subject to large errors" according to the authors of ref 7. For reasons of completeness, we also report that ω_e and $\omega_e\chi_e$ values obtained with the ^{81}Br isotope differ from the ^{79}Br isotope, on the average, by 1.5 and 0.1 cm^{-1}, respectively. In particular the ω_e and $\omega_e\chi_e$ values of N−^{81}Br at the icMRCI/aug-cc-pV5Z(RCCSD(T)) are 673.8-(693.4) and 4.51(4.19) cm^{-1}.

Synopsis

Using icMRCI and RCCSD(T) methods in conjuction with a series of correlation-consistent bases ranging from double to quintuple ζ quality, we have calculated the spectroscopic constants of the ground X$^3\Sigma^-$ state of the NBr. The final D_e and r_e values obtained are 49.5 kcal/mol and 1.780 Å. The D_e values of NX species, X = F, Cl, Br, decrease regularly from F to Br by about 12 kcal/mol, allowing us to suggest an estimate of ∼35 kcal/mol for NI. The NBr molecule is slightly polar with a charge transfer of ∼0.1 e$^-$ from Br to N and a dipole moment of 1.07 D.

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