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# Multireference Configuration Interaction and Coupled-Cluster Calculations on the $X^3\Sigma^-$ , $a^1\Delta$ , and $b^1\Sigma^+$ States of the NF Molecule

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**ABSTRACT:** The  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  states of the NF molecule were examined by a variety of ab initio methods, including the newly developed multireference Brillouin-Wigner coupled-cluster technique. Using correlation consistent sets of triple- and augmented quadruple-quality, we constructed full potential energy curves obtaining dissociation energies and spectroscopic constants. It was reconfirmed that the  $X^3\Sigma^-$  binding energy is 77.0 kcal/mol, in contrast to recent experimental results claiming a value of about 61 kcal/mol. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 104: 458–467, 2005

**Key words:** multireference Brillouin-Wigner coupled cluster (MRBWCC); dissociation energies; vbL diagrams

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## Introduction

Continuing our effort to explore the performance of our newly developed state-specific multireference coupled-cluster method based on the Brillouin-Wigner resolvent (MRBWCCSD) [1–6] on various chemical problems of multireference nature, we focus presently on the theoretical treatment of the ground and the two low-lying excited states of the NF radical. Our method has been shown to be able to describe satisfactory such problems as the geometrical and electronic structure of the ozone molecule [5], the singlet O<sub>2</sub> system [6], the automerization of cyclobutadiene [7], the potential energy curves of the dihalogens F<sub>2</sub> [8] and IBr [9], the correct ordering of the near-degenerate states in CaC and ZnC [10], and the singlet-triplet splittings of CH<sub>2</sub> [5], SiH<sub>2</sub> [5], twisted ethylene [5], and the tetramethylenethane radical [11].

The NF molecule has gained considerable attention over the last years due to the existence of two metastable excited states ( $a^1\Delta$  and  $b^1\Sigma^+$ ) which can act as chemical energy storage sources [12, 13]. In part, this interest arose from the similarity to O<sub>2</sub> ( $a^1\Delta_g$ ), which is used for pumping the  $^2P_{1/2}$ - $^2P_{3/2}$  transition of atomic iodine in a successful demonstration of an efficient chemical laser [14].

Milligan and Jacox [15] were the first to observe the infrared spectrum of NF trapped in an argon matrix. The  $b^1\Sigma^+$ - $X^3\Sigma^-$  and  $a^1\Delta$ - $X^3\Sigma^-$  transitions of this radical were subsequently detected by Douglas and Jones [16] and Jones [17], respectively, who also reported the usual spectroscopic parameters of the  $X^3\Sigma^-$  and the  $b^1\Sigma^+$  states.

A number of studies concerning the production and observation of NF have been reported in the literature, such as the reaction of H with NF<sub>2</sub> [12], of F with HN<sub>3</sub> [18, 19], the addition of O<sub>2</sub> ( $a^1\Delta_g$ ) to a mixture of NH<sub>3</sub>+F [20], the use of a supersonic mixing reaction chamber with the F, F<sub>2</sub>, NH<sub>3</sub> system [21], the UV photodissociation of NF<sub>2</sub> [22], the reaction of F atoms with HNCO [23, 24], and the thermal or vibrational dissociation of N<sub>3</sub>F [25] or NF<sub>3</sub> [26]. The quenching rate constants of the excited states of NF have been investigated in detail by Setser and co-workers [27]; their work was extended by Schmidt [28] and by Manke et al. [29]. Radiative lifetimes were determined by several authors [12, 30, 31], while the Stark effect of NF ( $a^1\Delta$ ) was measured by Curran et al. [32] resulting in the determination of the dipole moment of this state,  $\mu = 0.37 \pm 0.06$  D. Far-IR laser magnetic resonance

spectra of  $a^1\Delta$  have also been reported [33] complementing the work of Curran et al. [32]. Information on highly excited 3d/4d  $1^3\Phi$ , 3p  $1^3\Sigma^+$ , and 3p  $1^1\Delta$  Rydberg states was obtained using multiphoton ionization spectroscopy [34]. The rotational spectrum of the  $b^1\Sigma^+$  state was reexamined by Kobayashi and Saito [35] with the use of microwave spectroscopy; their work provides accurate bond lengths and spectroscopic constants for the ground and the excited states of NF.

The situation, however, is less clear concerning the dissociation energy  $D_e$  of the ground state. Montgomery et al. [36] describe in a lucid way the uncertainty over the value of the dissociation energy in the literature, the latter ranging by more than 10 kcal/mol. Huber and Herzberg [37] favor the  $D_0 = 80.7$  kcal/mol value of O'Hare and Wahl [38], the JANAF thermochemical tables [39] list two values, 71.4 and 70.4 kcal/mol, while an upper limit of 83.3 kcal/mol was extracted by Du and Setser [23]. Finally, Di Stefano et al., published a series of papers [40] in which they investigated the line strength of the transitions. In their most recent publication [40d], they estimate the ground state dissociation energy to be  $60.7 \pm 1.5$  kcal/mol, in stark discrepancy with the previous experimental and theoretical (see below) findings.

Early theoretical treatments of NF include the configuration interaction (CI) calculations of Andersen and Öhrn [41] with a minimal basis set predicting a binding energy of 50.7 kcal/mol. Similar calculations were published by Ellis and Banyard [42], who reported the spectroscopic constants of the ground and several excited states of NF. A few years later, Havriliak and Yarkony [43] described theoretically the process ( $b^1\Sigma^+$ ,  $a^1\Delta$ ) $\rightarrow$  $X^3\Sigma^-$  using a methodology based on the Breit-Pauli approximation, while Bettendorf and Peyerimhoff [44] obtained a  $D_0$  value of 68.3 kcal/mol at the multireference MRDCI/DZP level, including the Davidson correction. Montgomery et al. [36], on the other hand, performed QCISD(T) calculations extrapolated to the complete basis set limit, yielding  $D_0 = 76.1 \pm 0.9$  kcal/mol, a value identical to that obtained by Pople et al.'s "Gaussian 2" method [45]. The most sophisticated ab initio treatment in the literature is that of Xantheas et al. [46]. Those authors performed multireference configuration interaction (MRCI) and coupled cluster [RCCSD(T)] calculations using the family of correlation consistent basis sets cc-pVnZ up to sextuple zeta quality ( $n = 6$ ) and up to quintuple zeta quality for the aug-cc-pVnZ sets, followed by a complete basis set (CBS)

extrapolation. Their best  $D_e$  estimate was  $76.6 \pm 1.3$  kcal/mol. In a following article for the NBr molecule [47], this value was corrected for the spin-orbit splittings of F, to a final value of 76.2 kcal/mol. Later calculations at the RCCSD(T) level in conjunction with CBS extrapolation performed by Ricca [48] predicted  $D_e = 76.62$  kcal/mol, thus corroborating the previous values [46, 47]. Finally, Harbison [49] recently reported on the dipole moments and energy separations of the  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  states of NF using a multiconfiguration quasi-degenerate perturbation method in conjunction with a triple-z basis set.

Given the increased interest that the NF molecule has attracted over the last years, it is rather surprising that an accurate, high-level first principles calculation on the excited states of this species is still missing from the literature. It is the purpose of the present work to examine in detail the  $a^1\Delta$  and  $b^1\Sigma^+$  states of NF by constructing full potential energy curves, using different methods and quantitative basis sets. In addition, and although we consider the dissociation energy of the  $X^3\Sigma^-$  state as a solved problem within chemical accuracy [46, 47], this state is reexamined in the light of a recently determined experimental  $D_e$  value [40d], casting some doubts on the results of Ref. 46. Finally, it is of interest to test the MRBWCCSD methodology vs. the standard RCCSD/RCCSD(T) single reference method and the well-established multireference CASSCF+CISD approach.

The outline of this work is as follows: in the next section we give some technical details, in the Results and Discussion we report our results and comment on each state separately, while some concluding remarks and a final synopsis are given in the last section.

## Methods and Calculation Details

Two correlation consistent basis sets were used in the present work: The cc-pVTZ and the aug-cc-pVQZ of Dunning and co-workers [50], generally contracted to [4s3p2d1f] and [6s5p4d3f2g], respectively. The latter contains one additional diffuse function for every angular momentum of the plain cc-pVQZ basis. Note that  $l = 3, 4$ , and  $5$  symmetries number 6, 10, and 15 Cartesian Gaussian functions, respectively.

For the NF molecule (isoelectronic to  $O_2$ ) the lowest electronic configuration  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 - 1\pi^4 5\sigma^2 2\pi_x^1 2\pi_y^1$  gives rise to three bound electronic

states, namely,  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$ . For technical reasons a reference wavefunction for the MRBWCCSD calculations was used, keeping the  $1\pi^4$  electrons doubly occupied, while always utilizing a reference space based on CASSCF(4,4) optimized molecular orbitals (see below). Our projected wavefunction,  $\Psi_a^p$ , is a linear combination of four reference determinants (the  $M_s = 0$  component of the triplet state is computed together with singlets):

$$\Psi_a^p = \sum_i C_i^a \Phi_i. \quad (1)$$

The wave-operator  $\hat{\Omega}_a$  relates this wavefunction to the "exact" wavefunction  $\Psi_a$  according to the relation:

$$\Psi_a = \hat{\Omega}_a \Psi_a^p \quad (2)$$

while the exact energy  $\varepsilon_a$  is given through the effective Hamiltonian,  $\hat{H}^{\text{eff}}$ :

$$\hat{H}^{\text{eff}} \Psi_a^p = \varepsilon_a \Psi_a^p. \quad (3)$$

The wave-operator  $\hat{\Omega}_a$  is subjected to the state-specific Brillouin-Wigner analog of the Bloch equation:

$$\hat{\Omega}_a = 1 + \hat{B}_a \hat{V} \hat{\Omega}_a \quad (4)$$

where  $\hat{V}$  is the perturbation operator in the Møller-Plesset partitioning of the Hamiltonian, and  $\hat{B}_a$  is the Brillouin-Wigner resolvent given by the formula:

$$\hat{B}_a = \sum_q \frac{|\Phi_q\rangle\langle\Phi_q|}{\varepsilon_a - E_q}. \quad (5)$$

The diagonalization of the  $4 \times 4$   $\mathbf{H}^{\text{eff}}$  matrix [3, 6] gives the MRBWCCSD energy for the  $a^{\text{th}}$  state. Finally, the recently developed a posteriori correction [5, 51] is applied, making the method almost size extensive.

For the cc-pVTZ basis, the zeroth-order reference space to be used in the MRBWCCSD calculation was optimized by distributing four electrons ( $2p_x^1 2p_y^1 2p_z^1$  on N and  $2p_z^1$  on the F atom) in four orbitals using the CASSCF method. This calculation will be referred to as CASSCF(4,4). Furthermore, and for this basis set only, it is computationally feasible to examine the performance of the MRBWCC method when iterative triples excitations are

included in the wavefunction [52], a calculation which will be denoted as MRBWCCSDT- $\alpha$ .

The same approach was adopted for the aug-cc-pVQZ basis as well. Owing to technical reasons we were unable to include connected triples in the MRBWCCSD calculation; however, by observing the trends in the cc-pVTZ basis, we were able to correct for the missing triples and give an estimate of certain properties. To ensure the overall credibility, MRBWCCSD results were monitored vs. standard multireference and single reference techniques. Specifically, a bigger CASSCF calculation was performed in which eight electrons ( $2p^3$  of N and  $2p^5$  of F) were freely distributed among six orbitals ( $1\pi_x$ ,  $1\pi_y$ ,  $5\sigma$ ,  $2\pi_x$ ,  $2\pi_y$ , and  $6\sigma$ ), yielding 28 CFs for the ground and 33 CFs for the  $a^1\Delta$  and  $b^1\Sigma^+$  states (state-averaged), denoted CASSCF(8,6). Dynamical valence correlation was obtained by using the CASSCF(8,6) wavefunction as a zeroth-order reference and allowing all singles and doubles replacements (CASSCF+1+2 = MRCI), keeping the  $\sim 1s^2$  core electrons of both atoms doubly occupied. The internal contraction scheme as implemented in the MOLPRO package [53] was employed, resulting in substantial computational savings (icMRCI). Multireference averaged coupled-pair functional (MRACPF) and second-order perturbation theory over the CASSCF(8,6) wavefunction (CASPT2) calculations were also performed. Core correlation effects were taken into account by correlating all the electrons ( $16e^-$ ) in the CI procedure (C-MRCI), while relativistic effects were estimated via the spin-free Douglas-Kroll approximation (DK-MRCI). Finally, we performed standard coupled-cluster calculations including singles and doubles excitations, without and with core electrons, RCCSD and C-RCCSD, respectively, with a perturbative estimation of triples, RCCSD(T) and C-RCCSD(T), the results of which are directly compared to those of MRBWCCSD and MRBWCCSDT- $\alpha$ . All our calculations were done under  $C_{2v}$  symmetry constraints.

For our purposes the aug-cc-pVQZ basis is considered adequate, while no attempt was made to correct for basis set superposition errors (BSSE). The size-nonextensivity error at the icMRCI is about 7.4 kcal/mol, or 1.7 kcal/mol at the icMRCI + Davidson correction (=+Q). The MRACPF calculation is in essence size extensive, the error being just 0.07 kcal/mol.

Full potential energy curves are constructed for the ground  $X^3\Sigma^-$  and the two excited  $a^1\Delta$  and  $b^1\Sigma^+$  states of NF at the MRCI level of theory; a large

portion of the potential energy curves around equilibrium was also constructed at the MRBWCCSD level. We report dissociation energies ( $D_e$ ), bond lengths ( $r_e$ ), energy separations ( $T_e$ ), and dipole moments ( $\mu$ ), as well as the usual spectroscopic constants ( $\omega_e$ ,  $\omega_e x_e$ , and  $\alpha_e$ ) obtained by a Dunham analysis.

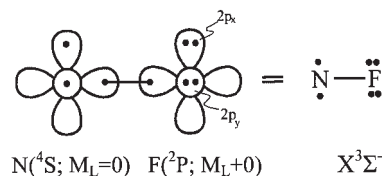
The CASSCF(4,4) calculations were performed using the Gaussian98 suite of codes [54]. For the MRBWCCSD and MRBWCCSDT- $\alpha$  calculations we used our own modified implementation of the ACESII program [55] with the restriction that the reference configurations can be no more than mutually biexcited. All other calculations were done with the MOLPRO package [53].

## Results and Discussion

Our results using the cc-pVTZ and the aug-cc-pVQZ basis are listed in Tables I and II, respectively. MRBWCCSD, MRCI/aug-cc-pVQZ potential energy curves are shown in Figures 1 and 2.

### $X^3\Sigma^-$ GROUND STATE

The leading CASSCF configuration of the NF  $X^3\Sigma^-$  state is  $|X^3\Sigma^- \rangle \sim 0.98 |1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 - 5\sigma^2 2\pi_x^1 2\pi_y^1 \rangle$ , described succinctly by the following valence-bond-Lewis (vbL) diagram:



showing the formation of a  $\sigma$ -bond. This is corroborated by the CASSCF(8,6) atomic populations at the MRCI equilibrium geometry,  $1s^2 2s^{1.84} 2p_x^{0.97} - 2p_y^{0.97} 2p_z^{0.65} /_N 1s^2 2s^{1.77} 2p_x^{1.59} 2p_y^{1.59} 2p_z^{1.11} /_F$  with the nitrogen atom exhibiting a small net effective charge of +0.1 and a dipole moment of 0.09 D, in accord with the value of 0.08 D predicted by Harbison [49]. Due to the essentially single reference character of the  $X^3\Sigma^-$  state, the MRBWCCSD method is expected to give similar results to RCCSD. Indeed, this is confirmed in the case of the cc-pVTZ basis, where the MRBWCCSD method improves slightly the bond distance, but yields results of a somewhat lower accuracy for the vibrational constants (see Table I). The situation changes significantly when

TABLE I

Total energies  $E$  (hartree), bond distances  $r_e$  (Å), dissociation energies  $D_e$  (kcal/mol), harmonic and anharmonic frequencies  $\omega_e$ ,  $\omega_e x_e$  ( $\text{cm}^{-1}$ ), rotational-vibrational constants  $\alpha_e$  ( $\text{cm}^{-1}$ ), and energy separations  $T_e$  ( $\text{cm}^{-1}$ ) of the  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  of the NF molecule at different methodologies. cc-pVTZ basis set.

Method	$-E$	$r_e$	$D_e$	$\omega_e$	$\omega_e x_e$	$\alpha_e$	$T_e$
<u><math>X^3\Sigma^-</math></u>							
CASSCF(4,4)	153.859 80	1.344	38.5				0.0
MRBWCCSD	154.239 20	1.312	67.1	1192	8.1	0.0138	0.0
MRBWCCSDT- $\alpha$	154.254 15	1.323	73.2	1142	9.2	0.0146	0.0
RCCSD <sup>a</sup>	154.234 32	1.313	66.4	1187	8.2	0.0141	0.0
RCCSD(T) <sup>a</sup>	154.248 31	1.320	71.4	1155	8.5	0.0144	0.0
Expt. <sup>b</sup>		1.31698	82.3 <sup>c</sup>	1141.37	8.99	0.01492	
Expt. <sup>d</sup>			70.4–82.3				
<u><math>a^1\Delta</math></u>							
CASSCF(4,4)	153.793 22	1.319	61.0				14611
MRBWCCSD	154.182 57	1.302	86.4 <sup>e</sup>	1236	8.1	0.0141	12429
MRBWCCSDT- $\alpha$	154.197 88	1.310	92.9 <sup>e</sup>	1193	9.4	0.0141	12350
Expt. <sup>b</sup>		1.3079					11435
Expt. <sup>f</sup>		1.30396		1181.73		0.01450	
Expt. <sup>g</sup>				1184	8.5		
<u><math>b^1\Sigma^+</math></u>							
CASSCF(4,4)	153.730 75	1.300	23.2				28322
MRBWCCSD	154.141 60	1.291	60.7 <sup>e</sup>	1265	7.8	0.0137	21421
MRBWCCSDT- $\alpha$	154.162 38	1.304	70.6 <sup>e</sup>	1206	7.7	0.0141	20143
Expt. <sup>b</sup>		1.29983		1197.49	8.64	0.01448	18877
Expt. <sup>f</sup>		1.29984		1197.55		0.01544	

<sup>a</sup> Reference 46.

<sup>b</sup> Reference 37.

<sup>c</sup> Reference 37.  $D_e = D_0 + \omega_e/2 - \omega_e x_e/4$ .

<sup>d</sup> References 23, 37–39.

<sup>e</sup> Estimated, see text.

<sup>f</sup> Reference 35.

<sup>g</sup> Reference 12.

the connected triples are included at the MRBWCCSDT- $\alpha$  level, yielding results which compare favorably to those obtained by the single reference RCCSD(T) method. For instance, the dissociation energy increases by 6.1 kcal/mol as contrasted to the MRBWCCSD value, 1.8 kcal/mol higher than the RCCSD(T), while the spectroscopic parameters are in very good agreement with the experimental ones.

The same pattern is also followed by the RCCSD and MRBWCCSD at the aug-cc-pVQZ level, both methods giving practically the same results (Table II). Although technical reasons prevented us from performing MRBWCCSDT- $\alpha$  calculations at this basis, we can give an estimate for the dissociation energy, assuming that the 6.1 kcal/mol difference

between the MRBWCCSD and MRBWCCSDT- $\alpha$  in the cc-pVTZ basis remains approximately the same. Thus, a  $70.9 + 6.1 = 77.0$  kcal/mol  $D_e$  value is obtained, in agreement with the C-RCCSD(T) and very close to C-MRCI+Q methods. This value is also in agreement with the previously reported one of  $76.6 \pm 1.3$  kcal/mol obtained by basis set extrapolation at the MRCI and RCCSD(T) levels [46], confirming that the “true” value of the dissociation energy is very close to 77 kcal/mol.

As expected, relativistic effects do not play any significant role, predicting negligible changes for all computed properties at both the MRCI and MRCI+Q levels, while core correlation seems to add 1.2 (1.4) and 1.6 kcal/mol at the C-MRCI (C-MRCI+Q) and C-RCCSD(T) levels, respectively, al-

TABLE II

Total energies  $E$  (hartree), bond distances  $r_e$  (Å), dissociation energies  $D_e$  (kcal/mol), harmonic and anharmonic frequencies  $\omega_e$ ,  $\omega_e X_e$  ( $\text{cm}^{-1}$ ), rotational-vibrational constants  $\alpha_e$  ( $\text{cm}^{-1}$ ), dipole moments  $\mu$  (Debye), and energy separations  $T_e$  ( $\text{cm}^{-1}$ ) of the  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  of the NF molecule at different methodologies, aug-cc-pVQZ basis set.

Method	$-E$	$r_e$	$D_e$	$\omega_e$	$\omega_e X_e$	$\alpha_e$	$\mu$	$T_e$
<u><math>X^3\Sigma^-</math></u>								
CASSCF(4,4)	-153.87230	1.343	39.0					0.0
CASSCF(8,6)	-153.88907	1.324	49.6				0.08	0.0
CASPT2	-154.28964	1.318	75.5	1135	8.4	0.0149	0.12	0.0
MRCI	-154.26997	1.316	72.3	1145	9.0	0.0149	0.09	0.0
MRCI+Q <sup>a</sup>	-154.29776	1.320	75.2	1134	7.6	0.0144		0.0
MRACPF <sup>b</sup>	-154.29431	1.320	74.4	1133	8.1	0.0149	0.07	0.0
DK-MRCI <sup>c</sup>	-154.38523	1.317	72.1	1141	7.1	0.0147	0.08	0.0
DK-MRCI+Q <sup>a,c</sup>	-154.41300	1.321	75.0	1134	8.3	0.0147		0.0
C-MRCI <sup>d</sup>	-154.34153	1.312	73.5	1155	8.1	0.0148	0.11	0.0
C-MRCI+Q <sup>a,d</sup>	-154.37359	1.316	76.6	1146	7.7	0.0143		0.0
RCCSD	-154.28468	1.310	70.0	1180	7.9	0.0141		0.0
RCCSD(T)	-154.30144	1.319	75.4	1144	8.4	0.0145		0.0
C-RCCSD <sup>d</sup>	-154.36123	1.306	71.5	1188	7.3	0.0138		0.0
C-RCCSD(T) <sup>d</sup>	-154.37855	1.314	77.0	1153	7.6	0.0141		0.0
MRBWCCSD	-154.28674	1.310	70.9	1186	7.9	0.0138		0.0
RCCSD(T) <sup>e</sup>	-154.31377	1.316	76.2 <sup>f</sup>	1152.7	8.6	0.0145		
Expt. <sup>g</sup>		1.31698	82.3	1141.37	8.99	0.01492		
Expt. <sup>h</sup>			70.4–83.3					
<u><math>a^1\Delta</math></u>								
CASSCF(4,4)	-153.80826	1.315	63.5					14055
CASSCF(8,6)	-153.82854	1.304	77.0				0.51	13286
CASPT2	-154.23917	1.307	98.9	1167	8.3	0.0148	0.50	11076
MRCI	-154.21740	1.302	96.1	1192	8.1	0.0144	0.44	11536
MRCI+Q <sup>a</sup>	-154.24633	1.308	98.4	1177	7.8	0.0142		11287
MRACPF <sup>b</sup>	-154.24328	1.307	97.9	1179	8.1	0.0143	0.40	11200
DK-MRCI <sup>c</sup>	-154.33267	1.303	95.9	1192	8.3	0.0148	0.44	11535
DK-MRCI+Q <sup>a,c</sup>	-154.36159	1.308	98.2	1177	8.3	0.0144		11283
C-MRCI <sup>d</sup>	-154.28878	1.298	97.5	1202	7.2	0.0144	0.47	11577
C-MRCI+Q <sup>a,d</sup>	-154.32209	1.302	100.0	1186	6.5	0.0140		11303
MRBWCCSD	-154.23195	1.298	91.5 <sup>k</sup>	1232	10.1	0.0150		12023
Expt. <sup>g</sup>		1.3079						11435
Expt. <sup>i</sup>		1.30396		1181.73		0.01450		
Expt. <sup>j</sup>				1184	8.5			
Expt. <sup>l</sup>							0.37 ± 0.06	
<u><math>b^1\Sigma^+</math></u>								
CASSCF(4,4)	-153.74346	1.298	22.9					28278
CASSCF(8,6)	-153.77834	1.298	45.5				0.81	24302
CASPT2	-154.20054	1.302	74.7	1179	8.5	0.0149	0.79	19554
MRCI	-154.17878	1.298	71.9	1208	8.5	0.0146	0.66	20014
MRCI+Q <sup>a</sup>	-154.21300	1.304	77.5	1193	8.1	0.0142		18601
MRACPF <sup>b</sup>	-154.20448	1.301	73.6	1195	8.4	0.0145	0.68	19716
DK-MRCI <sup>c</sup>	-154.29407	1.298	71.7	1207	8.4	0.0147	0.65	20007
DK-MRCI+Q <sup>a,c</sup>	-154.32826	1.304	77.3	1192	7.7	0.0143		18598
C-MRCI <sup>d</sup>	-154.24931	1.292	72.7	1217	7.6	0.0145	0.70	20238
C-MRCI+Q <sup>a,d</sup>	-154.28787	1.298	78.5	1202	7.2	0.0140		18813
MRBWCCSD	-154.19089	1.288	65.8 <sup>k</sup>	1257	7.5	0.0137		21035
Expt. <sup>g</sup>		1.29983		1197.49	8.64	0.01448		18877
Expt. <sup>l</sup>		1.29984		1197.55		0.01544		

<sup>a</sup> Including the Davidson correction.

<sup>b</sup> Multireference averaged coupled pair functional.

<sup>c</sup> Including Douglas-Kroll scalar relativistic corrections.

<sup>d</sup> Including the core  $1s^2$  electrons in the correlation procedure.

<sup>e</sup> RCCSD(T)/cc-pV6Z, best results, ref. 46.

<sup>f</sup>  $D_e$  from ref. 46 corrected for the spin-orbit interaction of F, ref. 47.

<sup>g</sup> Reference 37.

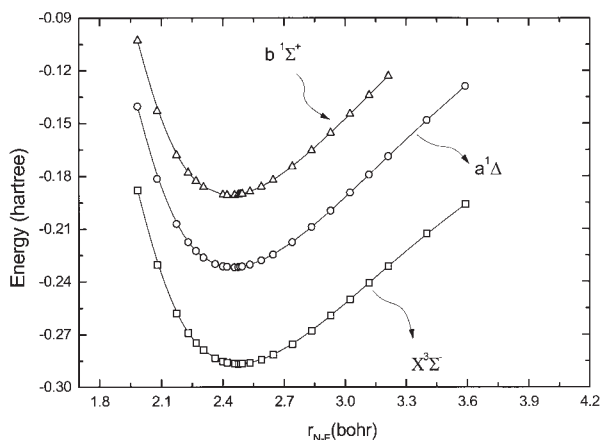
<sup>h</sup> Reference 23, 37–39.

<sup>i</sup> Reference 35.

<sup>j</sup> Reference 12.

<sup>k</sup> Estimated, see text.

<sup>l</sup> Reference 32.

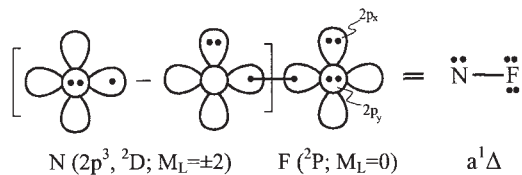


**FIGURE 1.** Potential energy curves for the  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  states of NF around equilibrium at the MRB-WCCSD/ aug-cc-pVQZ level of theory. All energies are shifted by +154.0 hartree.

though spectroscopic constants are less accurately predicted.

### $a^1\Delta$ STATE

The  $a^1\Delta$  state of NF correlates to  $N(^2D; M_L = \pm 2) + F(^2P; M_L = 0)$  fragments, with the following two leading equilibrium CASSCF configurations:  $|a^1\Delta\rangle \sim 0.69|(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 - 5\sigma^2)(2\pi_x^2 - 2\pi_y^2)\rangle$  or using vbL diagrams:

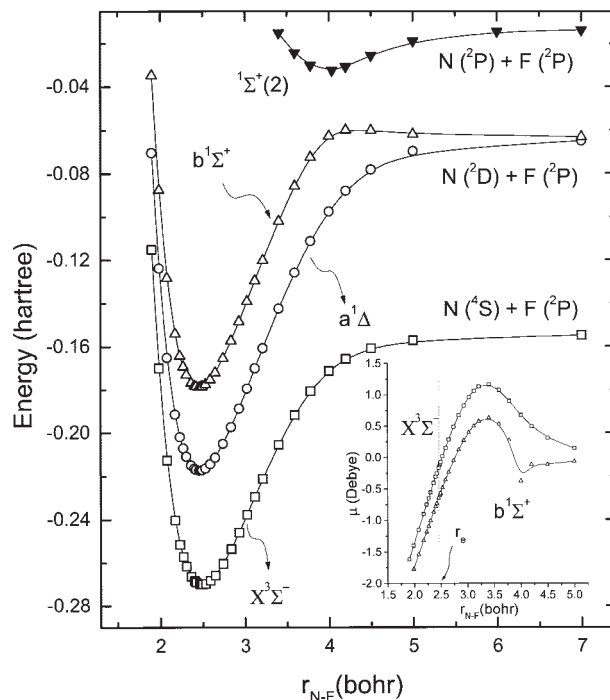


Clearly, the bonding occurs along the molecule's  $\sigma$ -frame in an analogous way as in the  $X^3\Sigma^-$  state, the difference being that the N atom now finds itself in its first excited  $^2D$  state, 2.384 eV above the  $^4S$  [56] or 2.430 (2.397) eV at the MRCI (+Q)/aug-cc-pVQZ level. The computed value of the dipole moment at the MRCI level is  $\mu = 0.44$  D, remaining practically unchanged when core correlation (0.47 D) or relativistic effects (0.44 D) are taken into account, in fair agreement with the experimental value of  $0.37 \pm 0.06$  D [32].

At the MRCI (+Q)/aug-cc-pVQZ level,  $D_e = 96.1$  (98.4) kcal/mol with respect to the adiabatic fragments, or 97.9 kcal/mol at the MRACPF level (Table II). DK-relativistic effects are practically

negligible ( $-0.20$  kcal/mol), while core effects add about 1.5 kcal/mol to the dissociation energy. Thus, our best estimate of  $D_e$  is very close to 99 kcal/mol at  $r_e$  (C-MRCI) (+Q) = 1.298 (1.302) Å;  $r_e$  (exptl) = 1.304 [35] and 1.308 [37]. Unfortunately, no experimental  $D_e$  results are available for the  $a^1\Delta$  state of NF. A  $T_e$  value of 11,536 (11,577)  $\text{cm}^{-1}$  is obtained at the MRCI (C-MRCI) level of theory, in very good agreement with the experimental number of 11,435  $\text{cm}^{-1}$  [35]. Again, DK-relativistic effects are negligible (Table II).

For technical reasons we were unable to calculate reliably the  $\Delta E(^2D \leftarrow ^4S)$  energy separation of N at the MRB-WCCSD method. An estimate of this value, though, was obtained by using the experimental  $\Delta E(^2D \leftarrow ^4S) = 2.384$  eV value [56]; therefore,  $E(N; ^2D) \approx -54.524$  au + 2.384 eV =  $-54.436$  au at the MRB-WCCSD/aug-cc-pVQZ level. Using this energy value, we estimate  $D_e \approx 92$  kcal/mol. Including the effects of triples from the cc-pVTZ basis (Table I),  $\delta D_e(\text{MRB-WCCSDT-}\alpha - \text{MRB-WCCSD}) \approx 6$  kcal/mol, a final value of

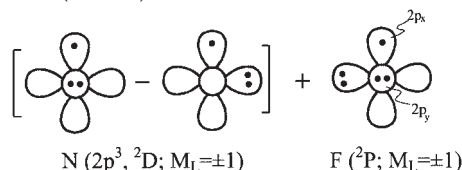


**FIGURE 2.** Potential energy curves of the  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  states of NF at the MRCI/ aug-cc-pVQZ level. The inset traces the dipole moments ( $\mu$ ) of the  $X^3\Sigma^-$  and  $b^1\Sigma^+$  states as a function of internuclear distance. All energies are shifted by +154.0 hartree.

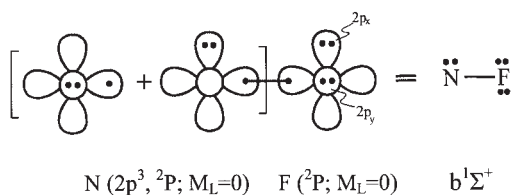
$D_e \approx 98$  kcal/mol is obtained, in agreement with the MRCI results.

### $b^1\Sigma^+$ STATE

The  $b^1\Sigma^+$  state traces its lineage to N ( $2p^3$ ,  $^2D$ ;  $M_L = \pm 1$ ) + F ( $^2P$ ;  $M_L = \mp 1$ ), or using vbL diagrams ( $r = \infty$ ):



The above approach gives rise to a repulsive  $^1\Sigma^+$  N + F interaction. However, at about 4 bohr an avoided crossing occurs with an incoming  $^1\Sigma^+(2)$  state originating from N ( $2p^3$ ,  $^2P$ ;  $M_L = 0$ ) + F( $^2P$ ;  $M_L = 0$ ), resulting to a bound  $b^1\Sigma^+$  state (Fig. 2). Therefore, at equilibrium the bonding character of the  $b^1\Sigma^+$  state is described by the following vbL icon:



showing that the two atoms are held together by a pure  $\sigma$  bond, very similar to the  $X^3\Sigma^-$  and  $a^1\Delta$  states. This attests to the fact that the bond lengths in all three studied  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$  states are practically the same (Table II). Mutatis mutandis, the situation is completely analogous to the  $X^3\Sigma_g^-$ ,  $a^1\Delta_g$ , and  $b^1\Sigma_g^+$  states of the isoelectronic  $O_2$  molecule, whose bond lengths among these states do not vary more than 0.02 Å [37].

At the MRCI (MRACPF) {C-MRCI}/aug-cc-pVQZ level the dissociation energy is  $D_e = 71.9$  (73.6) {72.7} kcal/mol with respect to the adiabatic fragments N ( $^2D$ ) + F ( $^2P$ ), with practically no contributions ( $-0.2$  kcal/mol) from DK-relativistic effects (Table II). However, the “intrinsic bond strength,” i.e., with respect to the diabatic atomic fragments N ( $^2P$ ) + F ( $^2P$ ), the  $D_e$  obtained is 103 kcal/mol at the MRCI level, very close indeed to the  $D_e$  value of the  $a^1\Delta$  state at the same level of theory (96.1 kcal/mol). Finally, taking also into account the Davidson correction, we can propose that the  $D_e$  value of  $b^1\Sigma^+$  state with respect to adiabatic

atoms should be close to 78 kcal/mol. Turning now to the MRBWCCSD and using the same assumptions as in the  $a^1\Delta$  section, we estimate that  $D_e \approx 76$  kcal/mol at the MRBWCCSDT- $\alpha$  level. At all levels of theory listed in Table II the bond distance is in excellent agreement with experiment [35, 37], while the best agreement with experiment concerning the  $T_e$  ( $b^1\Sigma^+ \leftarrow X^3\Sigma^-$ ) separation is calculated at the MRCI+Q or C-MRCI+Q level.

## Conclusions

The ground  $X^3\Sigma^-$  and the first two excited states  $a^1\Delta$  and  $b^1\Sigma^+$  of the NF diatomic were investigated employing a variety of methods, including the recently developed state-specific multireference Brillouin-Wigner coupled-cluster (MRBWCC) technique, coupled with triple and augmented quadruple quality basis sets.

The motivation of this work was twofold: 1) to reexamine the binding energy of the  $X^3\Sigma^-$  state due to very recent experimental findings suggesting a much lower  $D_e$  value ( $60.7 \pm 1.5$  kcal/mol [40d]) as compared to high-level ab initio findings [46, 47]; and 2) to test the MRBWCC method. Concerning question (1), our results show unequivocally that  $D_e = 77.0$  kcal/mol in complete agreement with the value reported in Refs. 46 and 47. Concerning question (2), the MRBWCC approach can cope fairly well in a difficult system such as the NF molecule, and we hope that by further development this method could become a useful tool in the general field of theoretical chemistry.

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