

A Theoretical Study of the Core-Ionized States of NF

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Abstract *Ab initio* spin-Unrestricted Hartree-Fock calculations are performed for the transition energies and vibrational coupling parameters associated to the core ionized states of NF. The vibrational excitation is discussed. Important aspects related to the ESCA band shapes and vibrational excitation are predicted but are not quantitatively described at this level of approximation.

1. INTRODUCTION

In recent years there has been an increasing research interest on the electronic structure of the NF radical¹⁻⁴. NF is isoelectronic to O₂ and possible analogies are of importance. It might also be used as the source of energy in the pumping process to produce atomic iodine chemical laser^{5,6}. Perhaps for these reasons most of the investigations have been directed to low-lying excited^{3, 7-11} and ionized states^{3,4}. On the inner region the electronic structure of NF has not deserved close attention so far; in particular, nothing is known about its core-ionized and core-excited states.

O₂ has long been a favourite system for study of paramagnetic molecules and was the first case of experimental detection of an exchange splitting¹² with two O_{1s} lines corresponding to quartet and doublet components separated by 1.1 eV and having a 2.47:1 intensity ratio. This deviation from the S(S+1):S intensity ratio¹³ comes both from differential orbital relaxation and correlation effects on the initial and final states¹⁴. From the theoretical viewpoint the existence of localized broken symmetry solutions has been of additional interest^{15,16}.

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We believe that an investigation of the core ionized states of the paramagnetic NF radical is also of sufficient interest to warrant a preliminary theoretical investigation despite the apparent absence of experimental data. We draw attention to some aspects related to vibrational excitation of the core ionized states via the vibrational coupling parameters¹⁷⁻¹⁸, calculation of the transition energies involved both for the core ionized and core excited states and we estimate within the frozen orbital approximation (FOA)¹⁹ the exchange splitting ${}^4\Sigma^-2\Sigma$ of both (N_{1s} and F_{1s}) core ionized states. Our computational resources are at present very limited. Therefore our study is at the Hartree-Fock level of approximation and further details particularly those related to many-body effects²⁰ and ESCA band shapes will be missing.

2. THEORETICAL ASPECTS

The ground state electronic configuration of NF is $1a^2 2c^2 3\sigma^2 4\sigma^2 1\pi^4 5a^2 2\pi_+ 2\pi_- \chi^3\Sigma^-$. Ejection of an inner shell electron yields quartet and doublet states. In the frozen orbital approximation¹⁹ one calculates the unrelaxed binding energy utilizing the orbital energy of the spin-Unrestricted Hartree-Fock (UHF) calculation on the neutral ground state. Due to large spin contamination on the doublet core ionized state we concentrate on the quartet state which is the highest spin multiplicity and therefore more appropriate to the UHF description. Values of $\langle S^2 \rangle_{UHF}$ will be given whenever convenient. As an estimate to the exchange splitting we calculate the difference in frozen orbital energies thus neglecting relaxation and the spin coupling among the open shells to produce the doublet multiplicity.

The basis set for both N and F consists initially of Dunning's (9s5p) contracted to <5s3p>²¹. Diffuse s and p functions as well as polarization d functions have been added and the final contracted basis set is <6s4p1d> for both atoms.

The energy of atomic nitrogen in the ground 4S state is -54.3990 h whereas the fluorine ground 2P state has the energy of -99.4013 h. The corresponding values of $\langle S^2 \rangle_{UHF}$ are 3.758 and 0.754, respectively. So, the spin contamination at the atomic level is not appreciable. At the calculated equilibrium geometry the NF ($\chi^3\Sigma^-$) has

the total energy of $-153.8277h$ thus amounting to a binding energy of 0.75 eV as compared to the near limit Restricted Hartree-Fock level which gives a value of $-0.7 \text{ eV}^{1,2}$. The $\langle S^2 \rangle_{\text{UHF}}$ value in this case is 2.022 again with a minor spin contamination. The binding energy of NF has not been measured directly but estimates indicate an experimental value of $-3.5 \text{ eV}^{1,2}$. An early CI calculation³ gave the binding energy as 2.2 eV . It may thus be deduced that our value for the binding energy is too small; this is not much surprising as correlation is expected to give an important contribution to the binding energy of NF^{1-3} . The equilibrium bond length is however in very good agreement. These data are collected in table 1 for comparison.

Table 1 - Spectroscopic parameters and energy of $\text{NF} (X^3\Sigma^-)$

	Present	Near Hartree-Fock Ref. 1,2	Ab initio CI Ref. 3	Experimental Ref. 7
E (h)	-153.8277	-153.8352	-153.2942	-
D_e (eV)	0.75	0.68	2.28	-
W_e (cm^{-1})	1242	1366	1265	1141
B_e (cm^{-1})	1.23	1.223	1.095	1.206
R_e (Å)	1.307	1.30	1.382	1.317

3. RESULTS AND DISCUSSION

In the table 2 we give the transition energies associated to the calculated $F_{1s} (1\sigma)$ and $N_{1s} (2\sigma)$ hole states. At the FOA level an energy of 715.57 eV is involved in the transition $^3\Sigma^- (\text{NF}) \rightarrow ^4\Sigma (\text{NF}^*)$. The calculated relaxation energy is obtained as 23.25 eV leading to a final binding energy of 694.22 eV . These values are typical of F_{1s} energies. The separate calculation of the NF^* core ionized state gives $\langle S^2 \rangle_{\text{UHF}} = 3.802$ indicating now a larger spin contamination. At the FOA level the $^2\Sigma$ state is estimated to lie slightly above with an exchange splitting of only -0.3 eV . The transition energy for $^4\Sigma (\text{N}^*\text{F})$ is 426.52 eV at the FOA level. Explicit calculation of this core hole state gives

a relaxation energy of 16.12 eV thus amounting to a prediction of 410.40 eV for the N_{1s} binding energy. Again, these values are typical of N_{1s} energies. The $\langle S^2 \rangle_{UHF}$ value of 3.886 indicates now a somewhat greater spin contamination. The exchange splitting estimated at the FOA level is 1.8 eV.

Table 2 - Transition energy (eV) of 1σ and 2σ electrons of NF at $R = 1.307 \text{ \AA}$.

Final state	$-\epsilon_i^{FOA}$ (eV)	ΔE_{SCF} (eV)	$\langle S^2 \rangle_{UHF}$
${}^4\Sigma$ (NF*)	717.54	694.22	3.802
${}^4\Sigma$ (N*F)	426.52	410.40	3.886
${}^3\Pi$ ($1\sigma \rightarrow 2\pi$)	-	686.03	2.028
${}^3\Pi$ ($2\sigma \rightarrow 2\pi$)	-	398.80	2.058

Also of interest are core-valence transition energies²². Table 2 also gives the values for the $1\sigma \rightarrow 2\pi$ (${}^3\Pi$) and $2\sigma \rightarrow 2\pi$ (${}^3\Pi$) states. These are calculated to lie below the corresponding quartet hole states by 8.19 eV and 11.60 eV, respectively. The spin contamination is mild for these core-valence states.

The vibrational coupling parameters are given in table 3 at both the one-particle level as well as including relaxation. In the case of N_{1s} ($-d\epsilon_{2\sigma}^{FOA}/dR$)₀ and ($-dE_{2\sigma}^{rel}/dR$)₀ partly cancel giving a final gradient of ($dE_{2\sigma}^*/dR$)₀ = 0.84 eV/bohr. This result ascribes an antibonding character to the 2σ molecular orbital and predicts a small bond length decrease, as expected from previously noted trends¹⁸. In the case of F_{1s} ($-d\epsilon_{1\sigma}^{FOA}/dR$)₀ and ($-dE_{1\sigma}^{rel}/dR$)₀ add to each other leading to a final value of ($dE_{1\sigma}^*/dR$)₀ = -5.32 eV/bohr. Hence the 1σ molecular orbital of NF may be ascribed as bonding. The large value for this coupling parameter indicates a considerable bond length increase. In previous systems²³⁻²⁵ one has obtained that F_{1s} ionization may indeed lead to a considerable lengthening and may even lead to a dissociative state. To check this we have performed a calculation of potential energy curve for the ${}^4\Sigma F_{1s}$ ionized state. The result is a dissociative curve. However a considerable care must be taken now because as mentioned before (see

Table 3 - Gradients of orbitals and relaxation energies (eV/bohr) for the Hole-States of NF at $R = 1.307 \text{ \AA}$. (1 bohr = 0.52917 \AA , 1 hartree = 27.21 eV). Q refers to the quartet state. D refers to the doublet state.

		$-\frac{d\epsilon_i^{\text{FOA}}}{dR}$	$-\frac{dE_i^{\text{rel}}}{dR}$	$+\frac{dE_i^*}{dR}$
NF $(1\sigma)^{-1}$	Q	-2.13	-3.19	-5.32
	D	-3.32	-	-
NF $(2\sigma)^{-1}$	Q	+3.57	-2.73	+0.84
	D	+3.72	-	-

table 1) we have obtained only a small percentage of the expected binding energy of the neutral ground state of NF. Hence one may not discard the possibility of a minimum hidden by the absence of correlation effects in our study. Similarly our explicit calculation of the $^4\Sigma N_{1s}$ core hole state gave a small bond length contraction but a fairly shallow potential energy curve. At any rate both explicit calculations reinforce a bond length shortening for the ionization of the 2σ and lengthening for the ionization of the 1σ molecular orbitals. This is also in due agreement with Ågren's analysis²⁶ based on the potential model for ESCA shifts which predicts opposite directions for the geometrical relaxation in diatomics.

The table 3 also indicates that each spin component for a particular core level exhibits different slopes. Hence the ratio of linewidths should be different from 1.0 indicating that one spin component state should be broader than the other one. At the FOA level one obtains that for both hole states the high energy doublet component is broader than the low energy quartet. That multiplet spin components of paramagnetic molecules should not be expected to be the same has been well demonstrated elsewhere¹⁵. It is also clear from that study that a theoretical model beyond the FOA level is however of essential importance for quantitative descriptions.

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Resumo

Cálculos ab initio ao nível UHF (Spin-Unrestricted Hartree-Fock) são feitos para as energias de transição e parâmetros de acoplamento vibracional associados aos estados ionizados em camadas profundas do radical NF. A excitação vibracional é discutida. Importantes aspectos relacionados com a forma da banda ESCA e excitação vibracional são previstos embora não sejam quantitativamente descritos a este nível de aproximação.