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SCF AB INITIO TREATMENT OF VERTICAL EXCITATIONS IN HNO AND FNO MOLECULES*, **

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SCF ab initio calculations have been carried out for the ground state and the lowest excited states of type $^1A'$, $^3A'$, $^1A''$, $^3A''$ for FNO and HNO molecules. The relaxation energy of the various excited states has been discussed. It has been shown that reoptimization of doubly occupied orbitals in the excited states plays almost always the most significant role. Population analysis for excited states has been given and the nature of bonding in excited states of FNO and HNO molecules has been discussed.

1. Introduction

The purpose of this work is to present results of SCF calculations performed for the ground and excited electronic states of nitrosyl fluoride (FNO) and nitroxyl (HNO) molecules. There is a very limited number of experimental and theoretical works dealing with the excited states of these molecules, particularly in the case of FNO molecule. The only known vertical electronic transition in this molecule occurs at 3.99 eV (Johnston and Bertin [1]). It has been tentatively assigned by Ditchfield et al. [2] as due to excitation from the highest occupied orbital $10a'$ to the lowest empty one, $3a''$, corresponding thus to the transition $^1A' \rightarrow {}^1A''$.

In the case of the HNO molecule there are three values of the vertical excitation energies known from experiment: 0.80 eV [3], 1.63 eV [4] and 5.98 eV [5]. The first two of them have been designated as the triplet and singlet electronic transitions from the ground state configuration to the singly excited one, $(7a' \rightarrow 2a'')^{3,1}A''$. The transition at 5.98 eV has been tentatively assigned by Wu, Buenker and Peyerimhoff on the basis of an extensive CI study [6] as the excitation from the ground state to the $(6a' \rightarrow 2a'')2^1A''$ excited one.

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2. Method

All the calculations reported here were performed using a modified 2×2 rotation method, designed for excited states SCF calculations of molecules with a closed-shell ground state [7]. The proposed method differs from that developed originally by Rossi [8] in that the orthogonality constraints are imposed on the total wave-functions in a different way. In Rossi's method the Lagrange multipliers technique is applied with this purpose while in the other method the 2×2 rotations are restricted from the very beginning to those which do not influence the orthogonality of the different states. Rossi's approach might yield a slightly better energy of the appropriate excited states. The alternative approach, however, is simpler and its convergence is definitely much more smooth.

3. Calculational details

The POLYATOM system of programs was applied for the ground state SCF calculations. Self consistent field calculations for the excited states were performed using the SCFEXC program elaborated in this laboratory [7]. All calculations were carried out on the CDC CYBER 72 computer in the Cracow Computer Center (CYFRONET).

The Gaussian basis sets used for fluorine, oxygen and nitrogen atoms were those of the 2ζ quality proposed by Huzinaga [9]: $\langle F|3,3,2,3;3,3\rangle$, $\langle 0|3,3,2,3;3,3\rangle$, $\langle N|3,3,2,3;3,3\rangle$. The basis set for the hydrogen atom was that suggested by Ahlrichs: $\langle H|3,1,1;1\rangle$ [10].

Experimental ground state equilibrium geometry was assumed taking the structural parameters of FNO over from Durig and Lord [11] ($R_{NO} = 2.135$ a. u., $R_{NF} = 2.872$ a. u., $\measuredangle$ FNO = 110°) and of HNO from Dalby [12] ($R_{NO} = 2.288$ a. u., $R_{NH} = 2.007$ a. u., $\measuredangle$ HNO = 108.5°).

4. Results of ground state SCF calculations

(*i*) The nitrosyl fluoride molecule

Ground state SCF calculations for this molecule have been reported already by Petrongolo, Srocco and Tomassi [13], Buenker and Peyerimhoff [14] and Ditchfield, Del Bene and Pople [2]. Comparison of our results with those obtained by the other authors is given in Table I. It follows from this table that results of the present SCF calculations are the best; the total energy is now only 0.08, eventually 0.18 a. u., away from the Hartree-Fock limit [14] and the dipole moment calculated is now closer to the experimental value than in the other cases.

In spite of using a basis set of a relatively good quality the binding energy due to these calculations remains still negative at the SCF level. This failure to predict the binding energy is evidently due to a significant change of the correlation energy during the dissociation into atoms.

Results of the population analysis for the ground state of FNO can be found in Table IV. According to the less accurate SCF calculations of Buenker and Peyerimhoff [14] there should be almost no bonding between the fluorine and nitrogen atoms. This conclusion

TABLE I

SCF results for the ground state of FNO (in a. u.)

Property[a]	This work[b]	Petrongolo et al. [13][b] min. STO	Buenker and Peyerimhoff [14][b] GLF	Ditchfield et al. [2][c] STO–31G	Experiment
Total energy[d]	−228.4493	−227.7084	−228.3800	−228.2823	−229.83 [14]
Binding energy	−0.160	—	−0.180	—	0.283 [1] 0.327 [19]
$-V/T$	2.000006	1.9891	1.9978	—	
μ	0.3986	0.1380	0.2877	—	0.7142 [20]
x	−0.3712	0.0393	−0.2658	—	−0.6711
y	0.1452	0.1323	0.1101	—	0.2443
$Q(\mathrm{CM})_{xx}$	−12.6541	—	—	—	—
$Q(\mathrm{CM})_{yy}$	−13.2589	—	—	—	—
$Q(\mathrm{CM})_{zz}$	−11.0689	—	—	—	—
$Q(\mathrm{CM})_{xy}$	0.4995	—	—	—	—
$\theta(\mathrm{N})^{\mathrm{d}}_{xx}$	16.3815	−10.20	−13.4362	—	—
$\theta(\mathrm{N})^{\mathrm{d}}_{yy}$	−18.6180	−10.67	−11.0682	—	—
$\theta(\mathrm{N})^{\mathrm{d}}_{zz}$	2.2366	−8.96	−12.9357	—	—
$\theta(\mathrm{N})^{\mathrm{d}}_{xy}$	0.0000	−0.21	−0.3235	—	—
Orbital energies					
$1a'$	−26.2978	−26.1669	−26,2801	—	—
$2a'$	−20.8266	−20.6753	−20.8744	—	—
$3a'$	−15.9782	−15.7569	−16.0316	—	—
$4a'$	−1.7632	−1.5938	−1.7718	—	—
$5a'$	−1.5787	−1.4350	−1.5808	—	—
$6a'$	−1.0150	−0.8653	−1.0219	—	—
$7a'$	−0.8380	−0.6739	−0.8460	—	—
$8a'$	−0.7918	−0.6162	−0.7924	—	—
$1a''$	−0.7811	−0.6085	−0.7877	—	—
$9a'$	−0.6510	−0.4587	−0.6547	—	—
$2a''$	−0.6439	−0.4528	−0.6487	—	—
$10a'$	−0.5349	−0.3335	−0.5390	—	—

[a] dipole moment, $Q(\mathrm{CM})$ — molecular second moment (relative to the center-of-mass), $\theta(\mathrm{N})$ — molecular quadrupole moment (relative to the position of nitrogen atom). [b] For ground state equilibrium geometry. [c] For optimized geometry. [d] Hartree-Fock limit: −228.53, −223.63 [14].

is partly confirmed. According to the present calculations the total bond population of the N-F bond (0.2157) is in fact much smaller than in the case of the bond N-O (0.6581), but still it is not negligible. As expected, fluorine and oxygen atoms are negative, nitrogen atom is largely positive (+0.415). The latter results differ significantly from the earlier and more approximate SCF calculations of Petrongolo et al. [13].

(*ii*) The nitroxyl molecule

SCF results obtained for the ground state of the HNO molecule are summarized and compared with other results in Table II. The best among the reported total energy values (−129.7344 hartree), obtained with a very extended basis set, is still 0.035 hartree lower than the value found in this calculations. Our result, on the other hand, is lower than the remaining ones by 0.102–0.785 hartree.

TABLE II

SCF results for the ground state of HNO molecule (in a. u.)

Property [b]	This work CG/RHF	Wu et al. [6] GLF/RHF	Brown and Williams [21] STO-3G/UHF	Solotto and Burnelle [18] [a] unc.CG/UHF	Ditchfield et al. [2] [a] STO-4G/RHF	Experiment
Total energy	−129.6990	−129.7344	−128.9139	−129.5966	−128.9840	
Dipole moment	0.4562	—	0.5890	—	—	0.6571 [22]
$Q(\mathrm{CM})_{xx}$	−9.7415	—	—	—	—	—
$Q(\mathrm{CM})_{yy}$	−10.4064	—	—	—	—	—
$Q(\mathrm{CM})_{zz}$	−8.1219	—	—	—	—	—
$Q(\mathrm{CM})_{xy}$	−0.0859	—	—	—	—	—
$\theta(\mathrm{CM})_{xx}$	0.3755	—	0.9056	—	—	—
$\theta(\mathrm{CM})_{yy}$	−1.7528	—	−2.3053	—	—	—
$\theta(\mathrm{CM})_{zz}$	1.3773	—	1.3963	—	—	—
$\theta(\mathrm{CM})_{xy}$	−2.8239	—	2.0005	—	—	—
Orbital energies						
$1a'$	−20.6760	−20.644	—	—	—	—
$2a'$	−15.7547	−15.727	—	—	—	—
$3a'$	−1.5577	−1.568	—	—	—	—
$4a'$	−1.0049	−1.003	—	—	—	—
$5a'$	−0.7471	−0.751	—	—	—	—
$6a'$	−0.6590	−0.663	—	—	—	—
$1a''$	−0.6058	−0.600	—	—	—	—
$7a'$	−0.4467	−0.440	—	—	—	—

[a] For optimized geometry. [b] Q — molecular second moment, θ — molecular quadrupole moment, for global coordinates), CM — relative to the center-of-mass.

The binding energy at the SCF level is negative again, similarly as it was in the case of the FNO molecule.

Results of the population analysis for the HNO molecule are presented in Table VI. In the case of FNO the bond population for the bond N-F was much smaller than for the bond N-O. In HNO bond populations for both bonds are comparable, being equal to 0.6970 for N-O and 0.5554 for H-N. In FNO the positive charge is located at the nitrogen atom. In HNO, on the other hand, the whole positive charge is located at the hydrogen atom, the nitrogen atom being now slightly negative.

5. *Vertical excitation energies*

(*i*) The FNO molecule

Vertical excitation energies corresponding to electronic transition from the ground state to the $^{1,3}A''$ and $^{1,3}A'$ lowest lying excited states were calculated within the framework of the SCF theory, taking care to the orthogonality constraints of excited states to the ground state. Results obtained are given in Tables III and IV. There is a rather limited possibility of comparing these results to those of other calculations or with experiment. The only nonempirical calculations concerning the excited states of FNO seem to have been reported by Ditchfield et al. [2]. They carried out limited CI calculations for adiabatic transitions to the $^{1,3}A''$ lowest lying excited states using a minimal orbital basis set (method STO — 31G). Their result for singlet transition of this symmetry (2.84 eV) is in moderate agreement with the experimental value 3.72 eV [1]. No information concerning calculated vertical excitation energies is available from their work. Our SCF result for the $^1A' \rightarrow {}^1A''$ vertical excitation energy (3.03 eV) is about 0.9 eV lower than the experimental value 3.99 eV [1]. Limited CI calculations, with 15 singly excited configurations for both states and 1 doubly excited configuration for the $^1A'$ state, increased this value to 3.70 eV, in good agreement with experiment [15].

TABLE III

Calculated vertical excitation energies for the FNO molecule

Excited state	Vertical excitation energy (in eV)		
	This work, SCF	This work, CI[a]	Experiment [1]
$(10a' \rightarrow 3a'')\ ^1A''$	3.03	3.70	3.99 (maximum)
$(10a' \rightarrow 3a'')\ ^3A''$	1.77	—	
$(2a'' \rightarrow 3a'')\ ^1A'$	4.71	4.22	3.72(0−0)
$(2a'' \rightarrow 3a'')\ ^3A'$	3.30	—	

[a] According to a limited CI study to be reported elsewhere [15].

Several interesting conclusions can be drawn from the population analysis carried out for the excited states (Table IV).

TABLE IV

Mulliken population analysis for the FNO molecule

	Ground state		Excited states			
	This work	Petrongolo et al. [13]	${}^{1}A''$ ${}^{1}(10a' \rightarrow 3a'')$	${}^{3}A''$ ${}^{3}(10a' \rightarrow 3a'')$	${}^{1}A'$ ${}^{1}(2a'' \rightarrow 3a'')$	${}^{3\prime}A'$ ${}^{3}(2a'' \rightarrow 3a'')$
Net atomic charge						
O	−0.1636	−0.0459	−0.1208	−0.1459	−0.2908	−0.2560
N	0.4152	0.0960	0.1975	0.2615	0.1681	0.2041
F	−0.2516	−0.051	−0.0767	−0.1157	0.1227	0.0519
Total orbital population						
O_σ	6.9988	6.7733	6.5382	6.5636	6.7726	6.8206
O_π	1.1648	0.9153	1.5825	1.5823	1,5182	1.4352
N_σ	5.7092	5.6270	5.3649	5.3005	5.3938	5.3841
N_π	0.8756	0.7677	1.4377	1.4379	1.4381	1.4119
F_σ	7.2920	6.9784	7.0970	7.1359	7.8336	7.7951
F_π	1.9597	1.9543	1.9798	1.9798	1.0437	1.1529
Total overlap population						
$(O-N)_\sigma$	0.2206	0.4013	0.4145	0.4466	0.5286	0.4839
$(O-N)_\pi$	0.4375	0.3477	0.0191	0.0195	0.0029	−0.0230
$(N-F)_\sigma$	0.1953	0.2523	0.2454	0.2695	−0.2541	−0.1865
$(N-F)_\pi$	0.0204	0.0175	−0.0245	−0.0244	−0.0123	0.0150
$(O-F)_\sigma$	−0.1252	−0.0322	−0.0962	−0.1047	−0.1082	−0.1120
$(O-F)_\pi$	−0.0171	−0.0025	−0.0079	−0.0079	0.0070	0.0125

The excitation $10a' \rightarrow 3a''$ is a $n \rightarrow \pi^*$ excitation. It is associated with a strong charge transfer from F to N and a smaller one from O to N. The charge transfer is stronger in the case of the singlet-singlet excitation than in the case of the singlet-triplet one. After the excitation the N-F σ bonding is getting slightly stronger and the anyway negligible N-F π bonding-weaker. The same is true, to a larger extent, in the case of the N-O bond; in these excited states the σ bond is now much stronger and the N-O π bond is almost broken.

The excitation $2a'' \rightarrow 3a''$ is a $\pi \rightarrow \pi^*$ excitation. The charge transfer relations are now much different. There is now a strong charge transfer from F to both, N and O, with a preference of N. Again, the σ O-N bonding is getting stronger, even to a larger degree than in the former case, the N-O π bonding is being broken. There is an opposite effect, however, in the change of bond populations in the case of the N-F bonding. In the former case the σ bonding increased. Now it changes sign, getting largely negative; the π-type bond population remains negligible. One might thus expect a complete break down of the F-N bond.

There are thus some reasons to believe that the excited states $(10a' \rightarrow 3a'')\ {}^{1,3}A'$

are still geometrically stable thereas that the excited states $(2a'' \rightarrow 3a'')\ {}^{1,3}A'$ are unstable, leading to dissociation of fluorine.

The most striking fact in the case of SCF-type calculations for excited states of the FNO molecule is a surprisingly high value of relaxation energy in some of these states (see Table VII). By relaxation energy we mean here the energy difference between the excited state defined by ground state SCF occupied and virtual orbitals and the excited state defined by re-optimized orbitals in the variational SCF procedure for excited states. In the case of $(2a'' \rightarrow 3a'')A'$ excited states the relaxation energy amounts to 6.65 eV and 5.13 eV for singlet and triplet excited states, respectively [6]. More than 90% of the relaxation energy results from the reoptimization of the doubly occupied orbitals (see Table VII). Thus, unexpectedly, optimization of the excited orbital is definitely less significant than the optimization of "core orbitals" as often implicitly believed [16].

(*ii*) The HNO molecule

Two theoretical studies of vertical excitations of the nitroxyl molecule have been published most recently: by Williams [17] on the basis of equation-of-motion method (EOM), being equivalent to the restricted CI treatment, and by Wu, Buenker and Peyerimhoff [6] on the basis of an extensive CI study of the vertical excitations of HNO. The latter authors carried out also a conformational analysis of the excited states of HNO by means of the Roothaan open-shell SCF method. Energies of excitations to the lowest ${}^{1,3}A''$ excited states of HNO were reported for optimized geometries by Ditchfield et al. [2]. Rather limited information concerning the electronic excitations can be obtained from the UHF calculations of Solotto and Burnelle [18]; their work was devoted mainly to the analysis of the reaction path HNO → H+NO. Comparison of our results with those reported by other authrs is given in Table V. The very low value of the energy of the $(7a' \rightarrow 2a'')^3A''$ excited state is characteristic for all open-shell SCF calculations for this

TABLE V

Calculated vertical excitation energies for the HNO molecule

Excited state	Excitation energies (in eV)						
	This work SCF(2×2)	Wu et al. [6]SCF[a]	Wu et al. [6] CI	Williams [17][c] EOM	Solotto [18] UHF	Ditchfield [2] CI[b]	Experiment
$(7a' \rightarrow 2a'')\ {}^1A''$	1.37	0.6	1.60	2.04	1.45	1.69	1.63 [3]
$(7a' \rightarrow 2a'')\ {}^3A''$	0.07	0.06	0.71	0.68	—	0.20	0.80 [4]
$(7a' \rightarrow 8a')\ {}^1A'$	8.80	—	6.17	8.88	—	—	5.98 [5]
$(7a' \rightarrow 8a')\ {}^3A'$	7.67	4.7	—	—	—	—	—
$(1a'' \rightarrow 2a'')\ {}^1A'$	13.84	—	—	—	—	—	—
$(1a'' \rightarrow 2a'')\ {}^3A'$	3.45	2.6	5.30	7.39	—	—	—

[a] Values taken from Fig. 1 of Ref. [6]. [b] For adiabatic transitions. [c] Electronic configurations of excited states are not explicitly stated in this reference.

molecule [6, 18] and is due to different correlation energies in the ground and excited states. The calculated transition energy for the vertical excitation $^1A' \to {}^1A''$ was 1.37 eV. This value is in quite a good agreement with the experimental value (1.63 eV [4]) and the result of CI (1.60 eV [6]). The singlet-triplet splitting for $(1a'' \to 2a'')A'$ excited states is about 10.4 eV. Approximately the same splitting was estimated by Wu et al. [6].

Results of the population analysis for the excited states of HNO are listed in Table VI. The lowest excitation $7a' \to 2a''$ leads to a charge transfer from O to N, to a strengthening of the N-O σ-bonding and to a break down of the N-O π-bonding, at least as far as conclusions can be drawn from the change of bond populations. The N-H bond seems not to be influenced much by this excitation. The excitation next in turn, from $7a'$ to $8a'$, is associated with a very strong electron transfer both from oxygen and nitrogen atoms to the hydrogen atom; the net charge of the hydrogen atom is changing from +0.3 to −0.3 in the case of the singlet state. Also significant changes in bonding, as following from the bond population analysis, might be expected: a small increase of the bonding N-O is expected, mostly due to σ-electrons, and a very strong antibonding effect in the case of the N-H bond. Thus, similarly as it was in the case of FNO, a dissociation into NO and the rest may be expected in the orbitally second excited state. The nature of this antibonding effect is, however, completely different. In the case of FNO the expected decay into F+NO would be caused by a π-π^* excitation, in the case of HNO, on the other hand, the reason would lie in the $n-\sigma^*$ excitation.

TABLE VI

Mulliken population analysis for the HNO molecule

	Ground state	$^1A''$ $^1(10a' \to 3a'')$	$^3A''$ $^3(10a' \to 3a'')$	$^1A'$ $^1(2a'' \to 3a'')$	$^3A'$ $^3(2a'' \to 3a'')$
Net atomic charges					
O	−0.2379	−0.1672	−0.1852	−0.0361	0.0877
N	−0.0893	−0.1920	−0.1742	0.3064	0.2798
H	0.3272	0.3594	0.3595	−0.2702	−0.1921
Total orbital populations					
O_σ	7.1099	6.6047	6.6226	6.7882	6.8722
O_π	1.1279	1.5626	1.5626	1.2479	1.2155
N_σ	6.2240	5.7865	5.7620	5.9369	5.9317
N_π	0.8654	1.4055	1.4123	0.7568	0.7885
H_σ	0.6661	0.6088	0.6154	1.2750	1.1961
H_π	0.0067	0.0319	0.0251	−0.0047	0.0000
Total overlap populations					
$(O-N)_\sigma$	0.2928	0.5251	0.5378	0.4193	0.4298
$(O-N)_\pi$	0.4042	0.0635	0.0622	0.3935	0.3981
$(N-H)_\sigma$	0.5449	0.5685	0.5649	−0.9390	−1.1092
$(N-H)_\pi$	0.0105	0.0588	0.0478	−0.0077	−0.0066
$(O-H)_\sigma$	−0.2298	−0.1989	−0.2037	−0.1905	−0.1882
$(O-H)_\pi$	0.0024	−0.0045	−0.0039	−0.0020	−0.0017

TABLE VII

Relaxation effect for the excited states of FNO and HNO molecules (in eV)

Excited state	Vertical excitation energy		Relaxation energy	Contribution to the relaxation energy [b]			
	GSMO [a] basis set	ESMO [a] basis set		e_x/e_v	e_i/e_c	e_i/e_v	e_c/e_v
FNO							
$(10a' \rightarrow 3a'')\ {}^1A''$	3.640	3.029	0.611	0.038	0.355	0.005	0.231
${}^3A''$	2.556	1.772	0.784	0.041	0.592	0.002	0.149
$(2a'' \rightarrow 3a'')\ {}^1A'$	11.363	4.710	6.653	0.006	0.170	0.267	6.210
${}^3A'$	8.434	3.302	5.132	0.011	0.000	0.209	4.913
HNO							
$(7a' \rightarrow 2a'')\ {}^1A''$	1.653	1.366	0.287	0.081	0.068	0.009	0.128
${}^3A''$	0.331	0.066	0.264	0.106	0.051	0.005	0.102
$(7a' \rightarrow 8a')\ {}^1A'$	9.789	8.795	0.994	0.133	0.095	0.280	0.486
${}^3A'$	9.085	7.675	1.410	0.629	0.305	0.192	0.285

[a] GSMO — ground state molecular orbitals, ESMO — molecular orbitals of the excited state in question.

[b] Types of contributions: e_x/e_v — contribution due to optimization of the excited orbital (x) within the virtual orbital space, e_i/e_c — contribution due to optimization of the singly occupied orbital (i) within the doubly occupied orbitals space, e_i/e_v — contribution due to optimization of the singly occupied orbital (i) within the virtual orbital space, e_c/e_v — contribution due to optimization of the doubly occupied orbitals (e_c) by mixing them with virtual ones.

Analysis of the relaxation energy in excited states of the HNO molecule given in Table VII supports the conclusions drawn in Ref. [7] as to the relative importance of the reoptimization of doubly occupied orbitals in the SCF-type calculations for excited states.

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