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An *ab initio* Investigation of the Collective Phenomena Accompanying the Core Ionization in the Radical NO

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The influence of the reorganization effect of an electron system on potential energy curves of X-ray excited states of the radical nitric oxide has been investigated by the restricted Hartree–Fock method. A dominating role of this collective effect in forming fine vibrational structures in ESCA and X-ray K_α emission spectra of this radical has been shown by such calculations.

Key Words: X-ray states – NO-radical – ESCA and X-ray spectra

1. Introduction and Details of the Calculation

It is known that all collective phenomena accompanying an ionization process of a molecule may be formally divided into two groups: the reorganization effects connected with the readjustment of molecular orbitals upon the influence of a Coulombic vacancy, and many-body effects themselves. Under the calculation of an ionization potential by the Green's function approach, the first phenomena are represented by the first correction term to Koopmans' theorem's value, i.e., the difference between the Hartree–Fock energy and the Koopmans' theorem energy of the discussed ionic state of the reference molecule, and the other phenomena correspond to the correlation correction terms [1, 2].

In the case of *valence* shell ionizations these two correction terms are often of the same order of magnitude but have opposite signs and this provides a good agreement between the experimental and the Koopmans' theorem ionization potentials for valence shells. In its turn, the above makes it possible to calculate the potential energy surfaces $E_i(R)$ for the valence ionized states (i^{-1}) with a sufficiently good accuracy in the frozen orbitals approximation. For example, such calculations may be performed for molecules with closed shells by using the Koopmans' theorem at different nuclear coordinates R [3, 4]:

$$E_i(R) = E_0(R) - \varepsilon_i(R), \qquad (1)$$

where $E_0(R)$ is the total Hartree–Fock energy of the ground state, and $\varepsilon_i(R)$ is the respective one-electron energy.

In the case of *core* shell ionization the reorganization becomes the dominating collective phenomenon [3–7]. The influence of the collective phenomena on the potential energy curves of the X-ray excited states of the molecules with closed shells CO and N_2 [3, 5–7] was studied by self-consistent and Green's function approaches. It was shown, for instance, that in the case of O$1s$ ionization of the CO molecule the change of the equilibrium distance of the molecule is mainly caused by the reorganization of the molecular electron system under the influence of O$1s$ vacancy.

In the present paper the reorganization effect is investigated in ionization processes of core shells of the radical nitric oxide, the ground electronic state of which has the electron configuration with one unpaired electron on the antibonding molecular orbital $2p\pi^*(2\pi^*)$:

$$(1s\sigma_O)^2(1s\sigma_N)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(2p\pi^*)^1,\ {}^2\Pi.$$

The ionization of an inner shell electron results in a number of electronic states because of the coupling of the unpaired electron spins between the inner and valence shells. Thus the ionization of a nitrogen $1s$ electron ($\overset{*}{\mathrm{N}}\mathrm{O}$), or oxygen $1s$ electron ($\mathrm{N}\overset{*}{\mathrm{O}}$), results in ${}^3\Pi$ and ${}^1\Pi$ molecular ion states. In the frozen orbital approximation we have the following equations for the ion NO^+, ${}^1\Sigma^+$ $(2\pi^{-1})$:

$$E_{2\pi}(R) = E_0(R) - \varepsilon_{2\pi}(R) \tag{2a}$$

and for the $n\sigma$-shell ionized states $(n\sigma^{-1})$:

$$E_i(R) = E_0(R) - \varepsilon_i(R) + \begin{cases} 3/2\ K_{2\pi,i}(R) - \text{total spin } S = 0 \\ -1/2\ K_{2\pi,i}(R) - \text{total spin } S = 1. \end{cases} \tag{2b}$$

The ${}^3\Pi$–${}^1\Pi$ energy splittings, i.e., exchange ones, of 0.7 eV and 1.5 eV have been observed by using ESCA for $\mathrm{N}\overset{*}{\mathrm{O}}$ and $\overset{*}{\mathrm{N}}\mathrm{O}$ respectively [8]. Generally speaking, it is impossible to neglect the dependence of the exchange integral $K_{2\pi,i}$ on the nuclear coordinates when computing the equilibrium distance R_e and vibrational frequency ω_e of the X-ray ionized states of the NO radical, in spite of the fact that these integrals are small in comparison with the magnitudes of ε_{O1s} and ε_{N1s}. The results of the calculations of the potential energy curves of the ground and ionized states of the radical NO are listed in Table 1, where curve parameters R_e and ω_e are the equilibrium distance and vibrational frequency obtained by performing restricted Hartree–Fock (RHF) calculations, i.e., taking into account the reorganization. $\hat{R}_e$ and $\hat{\omega}_e$ are the same parameters calculated by using the one-particle harmonic approximation (OHA) for the excited states [2–4, 9–11], i.e., by means of Eq. (1). It is easy to see that the difference between the corresponding RHF and OHA parameters is due to the R-dependence of the exchange integral $K_{2\pi,i}$ and to reorganization which are taken into account by the RHF method only. In the same table the RHF and experimental [8] vertical ionization potentials are presented, both being in agreement within 4 eV. Then, theoretically computed curve

Table 1. The calculated potential energy curves of the radical NO, R_e and $\hat{R}_e$ in a.u., ω_e and $\hat{\omega}_e$ in eV

Parameter	NO, $^2\Pi$	$N\overset{*}{O}$, $^3\Pi$	$N\overset{*}{O}$, $^1\Pi$	$\overset{*}{N}O$, $^3\Pi$	$\overset{*}{N}O$, $^1\Pi$	NO^+, $^1\Sigma^+$
$\Delta\hat{R}_e$		2.1794		2.0050		1.9253
ΔR_e	0.0000	-0.0061		-0.1805		-0.2602
R_e	2.1855	2.2923	2.3321	2.1577	2.1734	2.0081
ΔR_e	0.0000	0.1068	0.1466	-0.0278	-0.0121	-0.1774
$R_{\text{exper.}}$[a]	2.1745					2.0070
$\hat{\omega}_e$		0.332		0.197		0.247
ω_e	0.253	0.219	0.209	0.255	0.242	0.302
$\omega_{\text{exper.}}$	0.236					0.295
$R_e(O_2^+)$[b]		2.3187				
$\omega_e(O_2^+)$[b]		0.233				
I[c]		544.98	545.63	414.29	415.89	10.70
$I_{\text{exper.}}$[d]		543.3	544.0	410.3	411.8	9.26[e]

[a] Experimental values from [15].

[b] Experimental values for $Z + 1$ ion O_2^+ from [15].

[c] RHF ionization potentials (in eV) computed at $R = 2.1745$, $E_0 = -129.1858$ a.u.

[d] Experimental ionization potentials in eV from [8].

[e] Experimental adiabatic ionization potential in eV from [16].

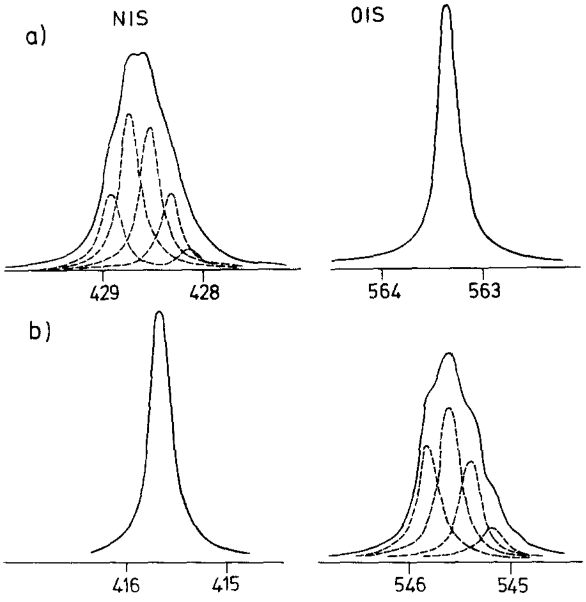

Fig. 1. The calculated NO ESCA spectrum (energy in eV, intensity in relative units): on the left side is the N1*s* spectrum, on the right side is the O1*s* spectrum. The used line width is 0.22 eV. (a) shows the intensity distribution calculated in OHA, (b) shows the intensity distribution calculated by RHF method (the states $^1\Pi$). RHF $^3\Pi$ – $^1\Pi$ energy splittings are 0.65 eV and 1.60 eV for $N\overset{*}{O}$ and $\overset{*}{N}O$, respectively

parameters were used to calculate the fine vibrational structures of O1*s* and N1*s* ESCA (Fig. 1) and X-ray NK_α emission (Fig. 2) and OK_α emission (Fig. 3) spectra of the NO radical in the harmonic approximation.

The double zeta Gaussian basis set (10*s*5*p*) was employed [12]. The calculations were performed by using the IBMOL-5 program [13] implemented on BESM-6. The contraction was as follows: *s*(3, 4, 2, 1) and *p*(4, 1). The motivation for employing this basis set was supplied by our experience in previously performed calculations on the core shell ionized states of the molecule CO [3].

2. Discussion

In the literature there are no experimental data with high resolution for the core shell ionized states of NO, therefore the above RHF calculations of the vibrational fine structure in O1*s* and N1*s* ESCA spectra are of a predictive character. The computed RHF fine vibrational structure of the X-ray NK_e emission spectrum of

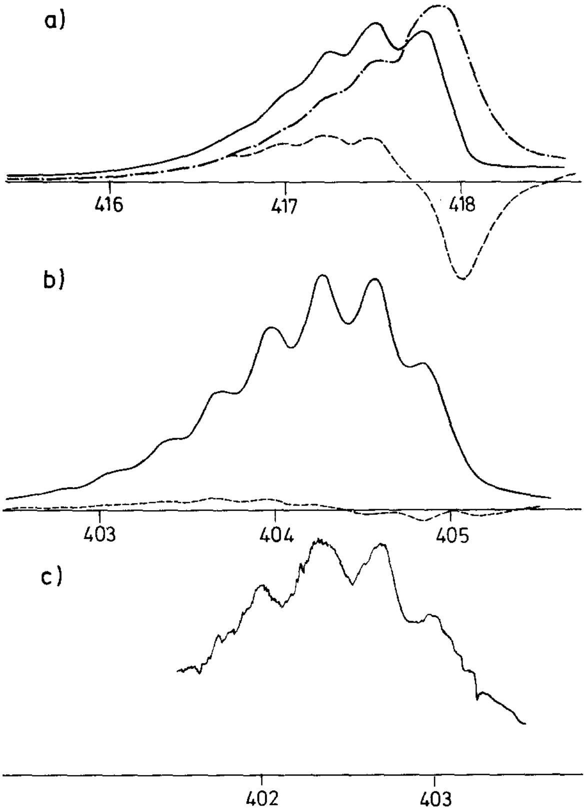

Fig. 2. The NK_α emission spectrum of the radical NO (energy in eV, intensity in relative units): the transition 2π — N1*s*, the used linewidth is 0.27 eV. (a) shows the intensity distribution calculated in OHA, (b) by the RHF method; (c) shows the experimental spectrum [14]

Table 2. The calculated Franck–Condon factors of ESCA spectra of the radical NO

Calculation		Vibrational component quantum number n										
State	Method	0	1	2	3	4	5	6	7	8	9	10
$O1s^{-1}$	OHA	0.99	0.002									
$O1s^{-1}, {}^3\Pi$	RHF	0.51	0.37	0.11	0.02	0.001						
$O1s^{-1}, {}^1\Pi$	RHF	0.29	0.39	0.23	0.08	0.01	0.002					
$N1s^{-1}$	OHA	0.17	0.33	0.30	0.15	0.05	0.01	0.001				
$N1s^{-1}, {}^3\Pi$	RHF	0.94	0.06	0.002								
$N1s^{-1}, {}^1\Pi$	RHF	0.99	0.004									
$NO^+, {}^1\Sigma^+$	OHA	0.01	0.06	0.13	0.19	0.20	0.17	0.12	0.07	0.04	0.02	0.007
$NO^+, {}^1\Sigma^+$	RHF	0.14	0.28	0.27	0.18	0.09	0.03	0.01	0.003			

NO is in good agreement with the shape of the experimental spectrum [14]. As the computed equilibrium distances and vibrational frequencies of the initial state NO, $^2\Pi$, and final state NO^+, $^1\Sigma^+$ in the electron–molecule inelastic scattering agree well with the known experimental values, it follows that the computed RHF curve parameters R_e and ω_e, for the intermediate N1*s* ionized state $\overset{*}{N}O$, $^1\Pi$, are close to the experimental values as well. These experimental parameters are not yet available in the literature. It follows that, as in the case of the molecules with closed shells CO and N_2, the correlation is negligible and the reorganization becomes the dominating collective phenomenon accompanying the core ionization in the radical NO.

The RHF energy of the state $\overset{*}{N}O$, $^3\Pi$ is less than that of the state $\overset{*}{N}O$, $^1\Pi$ in two exchange integrals $K_{2\pi,N1s}$. Tables 1 and 2 show that this results in a negligible difference between curve parameters R_e and ω_e of the two states and hence between the fine vibrational structures of their ESCA spectra. It means the *R*-dependence of the exchange integral $K_{2\pi,i}$ may be neglected in the case of the electron configuration $\overset{*}{N}O$, which leads us to suggest that the considerable difference between RHF curve parameters R_e and ω_e on the one hand, and OHA curve parameters $\hat{R}_e$ and $\hat{\omega}_e$ on the other hand, is mainly caused by the reorganization. In other words, the reorganization leads to the disappearance of the OHA extended fine vibrational structure in the N1*s* ESCA spectrum of the radical NO (Fig. 1).

There is a slightly greater difference between the RHF parameters R_e and ω_e for the O1*s* ionized states $N\overset{*}{O}$, $^3\Pi$, and $N\overset{*}{O}$, $^1\Pi$. Nevertheless, in this case the number of vibrational components with a considerable value of a Franck–Condon factor in the $N\overset{*}{O}$, $^3\Pi$, and $N\overset{*}{O}$, $^1\Pi$ structures is the same (Table 2) and it also gives us reason to believe that it is the reorganization that leads to the extended fine vibrational structure in the O1*s* ESCA spectrum of the radical NO (Fig. 1) and to the significant expansion of the structure in the OK_α emission spectrum (Fig. 3). Unfortunately, the X-ray OK_α emission spectrum of NO, with a well resolved fine vibrational structure, is not known yet.

As may be seen from Table 2 and Eq. (2a) the reorganization results also in the considerable reduction of the extended fine vibrational structure which was caused by a removal of an electron from the antibonding valence molecular orbital 2π in NO, i.e. OHA structure 2π.

An X-ray emission spectrum is the result of a resonant inelastic scattering which may go through different vibrational levels of the intermediate core shell excited state, i.e. in different scattering channels. In Figs. 2 and 3 the chain-dotted line (–·–·–·–) represents the leading term of the inelastic scattering contribution from different channels, the dashed line (– – – –) the term describing the interference among these channels. It is easy to see in Figs. 2 and 3 that the interference term is very susceptible to the form of the potential energy curves of the excited states of the radical NO.

The computed RHF curve parameters R_e and ω_e for the 1*s* nitrogen ionized states of NO are in good agreement with the corresponding experimental values for its

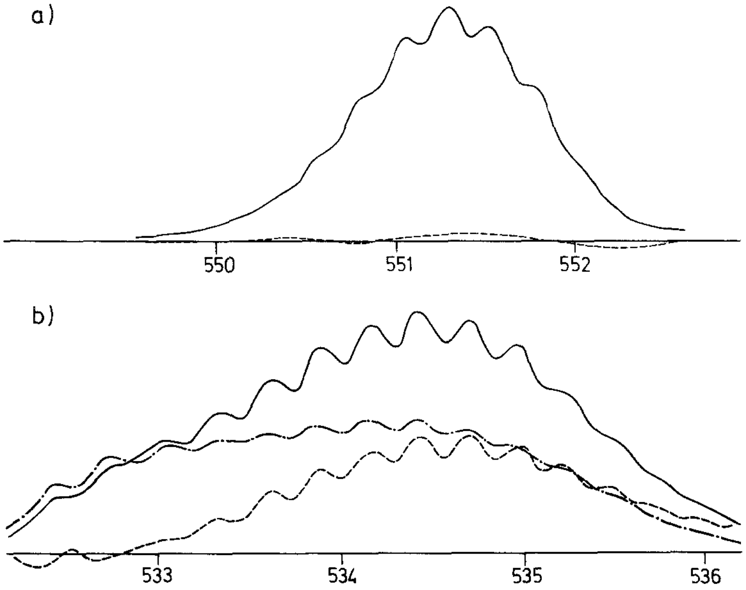

Fig. 3. The OK_α emission spectrum of the radical NO (energy in eV, intensity in relative units): the transition 2π — $O1s$, the used linewidth is 0.27 eV. (a) shows the intensity distribution calculated in OHA, (b) by the RHF method

$Z + 1$ ion O_2^+ [15]. This confirms the validity of using the $Z + 1$ model for the calculations of fine vibrational structures in ESCA and X-ray spectra of radicals. Thus, the RHF curve parameters of the $\overset{*}{NO}$ states presented in Table 1 may be considered an approximate estimate for corresponding parameters of the $Z + 1$ ion NF^+ which are not available in the literature.

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