

SOLID STATE EFFECTS ON CORE-HOLE SPECTRA**R.W. BIGELOW***Xerox Webster Research Center, Webster New York 14580 USA*

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Selective orbital coupling between levels of the ion and adjacent "neutral" molecules are shown to rationalize the spectral changes in the N 1s and O 1s XPS core-hole signals of *p*-nitroaniline on going from the vapor to condensed phase

Recently Domcke et al. [1–3] discussed the results of a many-body *ab initio* quantum chemical calculation on the shake-up states accompanying core ionization of the polar ($D^+ - Ar - A^-$) molecule *p*-nitroaniline (PNA) to exemplify from "first principles" the complex dynamical screening processes leading to multiplex structure in core-hole spectra. Briefly, Domcke et al. [1–3] assigned the high binding energy peak of the solid state N 1s (NO_2) doublet [4,5] to the primary core-hole, whereas the second lower binding energy peak was attributed to negative shake-up states arising from a superposition of the two possible doublet states — the "singlet" and "triplet" multiplets of the well characterized $\pi^* \leftarrow \pi$ charge-transfer excitations of the neutral molecule. N 1s (NH_2) ionization, on the other hand, was shown to selectively destabilize such transitions consistent with the absence of the low-energy shake-up structure associated with ionization of the donor nitrogen level. Although Domcke et al. [1–3] obtained an intensity distribution and splitting of the N 1s (NO_2) doublet structure in excellent correspondence with experiment, the core-hole state of O 1s and its accompanying satellite structure [4,5] was not treated.

More recently Banna [6] reported gas phase XPS measurements on PNA where it was found that the

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O 1s spectrum appeared only slightly modified from the solid phase results, whereas the nitrogen spectrum exhibited only the single components expected from the N 1s (NO_2) and N 1s (NH_2) primary core-holes. Based on the differences between the vapor and solid phase results and the computations of Domcke et al. where the assumed structure was that of a single unperturbed molecule (gas phase molecule) Banna concluded that negative shake-up in PNA and structurally related systems has not been unambiguously demonstrated.

The purpose of this letter is to show that *intermolecular* orbital coupling as a consequence of core-hole ionization serves to rationalize the spectral changes associated with the above phase transition. Particularly, we find that response of the valence orbital manifold to the N 1s (NO_2) core-hole in the condensed phase is not inconsistent with an interpretation based on negative shake-up states.

PNA has been well characterized as having a lowest unoccupied molecular orbital (LUMO) largely localized on the nitro group, whereas the highest occupied (HOMO) level is localized on the donor amino fragment. In agreement with the results of Domcke et al. [1–3] we find these levels to be the prime contributors to shake-up phenomena. The following treatment, therefore, emphasizes interactions involving these levels.

In terms of the closed-shell neutral molecule an elec-

tronic excitation leads to singlet and triplet configurations with energies [7],

$${}^1\tilde{E}_{\pi\pi^*} = \epsilon_{\pi^*} - \epsilon_{\pi} - J_{\pi\pi^*} + 2K_{\pi\pi^*} \quad (1a)$$

and

$${}^3\tilde{E}_{\pi\pi^*} = \epsilon_{\pi^*} - \epsilon_{\pi} - J_{\pi\pi^*}, \quad (1b)$$

where ϵ_{π} , ϵ_{π^*} are the orbital energies, and $J_{\pi\pi^*}$ and $K_{\pi\pi^*}$ are the Coulomb and exchange integrals, respectively. The excitation energies in the presence of r core-hole (ϵ_k) are [2],

$$\begin{aligned} {}^2\tilde{E}_{\pi\pi^*}^1(k) = & (\epsilon_{\pi^*} - J_{\pi^*k}) - (\epsilon_{\pi} - J_{\pi k}) - J_{\pi\pi^*} + 2K_{\pi\pi^*} \\ & + K_{\pi k} + \frac{1}{2}K_{\pi^*k} - \frac{3}{2}K_{\pi\pi^*} \end{aligned} \quad (2a)$$

and

$$\begin{aligned} {}^2\tilde{E}_{\pi\pi^*}^3(k) = & (\epsilon_{\pi^*} - J_{\pi^*k}) - (\epsilon_{\pi} - J_{\pi k}) - J_{\pi\pi^*} \\ & - [K_{\pi k} - \frac{3}{2}K_{\pi^*k} - \frac{3}{2}K_{\pi\pi^*}], \end{aligned} \quad (2b)$$

where ${}^2\tilde{E}_{\pi\pi^*}^1(k)$ and ${}^2\tilde{E}_{\pi\pi^*}^3(k)$ are the energies of the singlet- and triplet-coupled doublet states (${}^2\Psi_{\pi\pi^*}^1$ and ${}^2\Psi_{\pi\pi^*}^3$, respectively) and,

$$\Delta{}^2\tilde{E}_{\pi\pi^*}^{1,3}(k) = 2K_{\pi k} - K_{\pi^*k} - K_{\pi\pi^*}. \quad (3)$$

Due to spin selection rules the additional quartet state which can be constructed by appropriate combination of the three spins involved is not populated.

The terms in parentheses in eqs. (2) emphasize the electrostatic shifts [8] of the orbital eigenvalues due to the core-hole where, for example, $\Delta\epsilon_{\pi^*} = \epsilon_{\pi^*} - J_{\pi^*k}$. The nature of the orbitals implies that for a core-hole localized on the nitro group $J_{\pi^*k} \gg J_{\pi k}$, whereas a core-hole on the amino group yields $J_{\pi k} \gg J_{\pi^*k}$. In the former case ${}^2\tilde{E}_{\pi\pi^*}^{1,3}(k) < {}^1,3\tilde{E}_{\pi\pi^*}$ while in the latter situation ${}^2\tilde{E}_{\pi\pi^*}^{1,3}(k) > {}^1,3\tilde{E}_{\pi\pi^*}$. Also, since the oxygen atoms are on the perimeter of the molecule the stabilization interactions (J_{π^*k} and $J_{\pi k}$) should be weaker for O 1s ionization by a factor of R^{-1} relative to N 1s (NO_2) ionization. This suggests that shake-up

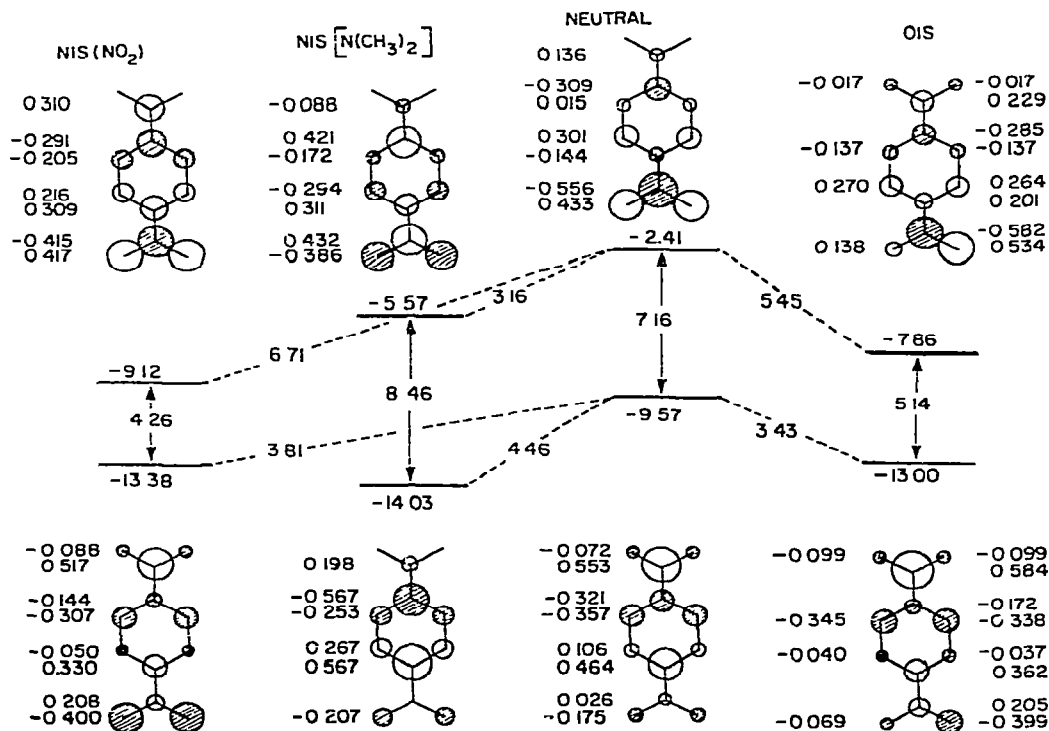


Fig. 1. A schematic representation of the HOMO and LUMO levels of the neutral and indicated ionic species as viewed from above the molecular plane (AO coefficients are given opposite the appropriate center). Also given are the energetics of the HOMO and LUMO shifts relative to the neutral molecule

excitations accompanying N 1s (NO₂) ionization will be energetically closer to the primary hole state than corresponding transitions in the presence of the O 1s core-hole. The gas phase results of Banna [6] reflect this rationalization.

Equivalent-core calculations [9–13] were performed within the CNDO/S framework [14] to simulate perturbations to the valence orbital manifold by selected core-holes. The energies and wavefunctions of the important one-electron levels (HOMO and LUMO) for the neutral molecule and the isolated ions are shown in fig. 1. Numerical calculations on the free N,N-dimethyl-*p*-nitroaniline (DMPNA) molecule, and the corresponding ions, were performed prior to the publication of Banna's spectra [6]. It was not considered necessary to duplicate the effort for PNA as the effect of methyl group substitution on the donor nitrogen would be of no consequence for the present purposes. Therefore, we directly compare our results for DMPNA with the PNA gas phase spectra. As expected the orbitals of the ions are shifted to lower binding energy relative to the corresponding levels in the neutral molecule due to the presence of the positive charge.

In line with our above analysis of eqs. (2) the selective orbital shift arising from a core-hole on the nitro group decreases the HOMO–LUMO gap more strongly for N 1s (NO₂) than for O 1s (NO₂) ionization. N 1s (NH₂) ionization, on the other hand, increases the HOMO–LUMO gap for obvious reasons [15]. The excitation energies for the ions were calculated by a standard configuration-interaction method where the 60 singly excited configurations of lowest energy were included. However, excitations in the closed-shell $Z + 1$ system are classified according to singlet and triplet character and, consequently, do not directly correspond to the doublet states of the ion. A comparison can nevertheless be achieved by assuming that the change in average configuration energy (\tilde{E}_{av}),

$$\tilde{E}_{av} = \frac{1}{4}\tilde{E}_{\pi\pi^*} + \frac{3}{4}\tilde{E}_{\pi\pi^*}, \quad (4)$$

upon creation of a core-hole calculated from the $Z + 1$ system is reasonably described. Since the multiplet splitting relative to \tilde{E}_{av} is given by eq. (3) the appropriate multiplet energies can be determined provided the exchange terms are known. The unique character of the π and π^* levels shown in fig. 1 suggest the simpli-

Table 1

The excitation energies (eV) of interest and shake-up intensities (²*P*) for the indicated gas phase species ¹ \tilde{E}_{CT} and ³ \tilde{E}_{CT} of the ions refer to the $Z + 1$ system parentage. (A) denotes values obtained from singly excited configurations arising from HOMO → LUMO excitation before configuration interaction, (B) denotes values obtained after configuration interaction (²*P*_{1,2}(B) values were calculated by restricting the CI expansion to the two largest elements), and (C) values after inclusion of the single doubly excited configuration

		N 1s (NO ₂)	N 1s [N(CH ₃) ₂]	O 1s (NO ₂)	Neutral
¹ \tilde{E}_{CT}	(A)	2.91	5.34	3.31	4.30
	(B)	2.78	5.19	3.20	4.14
³ \tilde{E}_{CT}	(A)	-0.45	3.73	0.82	3.43
	(B)	-0.71	3.00	0.23	2.83
<i>J</i> _{ππ*}	(A)	4.71	4.73	4.32	3.73
<i>2K</i> _{ππ*}	(A)	3.36	1.61	2.49	0.87
<i>E</i> _{av}	(A)	0.39	4.13	1.44	3.65
	(B)	0.16	3.55	0.97	3.16
² $\tilde{E}_{\pi\pi^*}^1$	(A)	1.59	5.33	2.64	
	(B)	1.36	4.75	2.17	
	(C)	1.60	4.78	2.33	
² $\tilde{E}_{\pi\pi^*}^3$	(A)	0.39	4.13	1.44	
	(B)	0.16	3.55	0.97	
	(C)	0.85	3.59	1.14	
² <i>P</i> _{ππ*} ¹	(A)	38.5	<0.1	22.6	
	(B)	37.4	<0.1	21.9	
	(C)	39.7	<0.1	24.1	
² <i>P</i> _{ππ*} ³	(C)	4.9	<0.1	4.6	

fication $K_{\pi^*k} \gg K_{\pi k}$ and $K_{\pi\pi^*}$ where k indicates a core-hole on the nitro-group. Within this approximation ${}^2E_{\pi\pi^*}^3(k)$ is given by E_{av} of the $Z+1$ system and ${}^2E_{\pi\pi^*}^1(k)$ by $E_{av} + K_{\pi^*k}$. K_{π^*k} is essentially an exchange interaction between an atomic $1s$ orbital and a valence π -orbital component of the π^* level, and it is expected that the experimentally observed splitting of the ionization in the free NO molecule (1.2 eV) [16] is a reasonable approximation.

It has recently been demonstrated for adsorbates [17,18] that coupling between the primary core-hole and the singly excited states is essential, under certain conditions, to the understanding of the core-hole spectra. This mixing appears particularly important in the case of $\text{N } 1s$ (NO_2) ionization where ${}^2E_{\pi\pi^*}^3 \approx \epsilon_k$. Although interaction between the ground and singly excited states vanishes in a closed-shell Hartree-Fock formalism, inclusion of doubly excited states permits such coupling [19,20]. Hence, we have chosen a single doubly excited configuration created by promoting both electrons from the HOMO into the LUMO to examine the effects of such mixing in the present case. This additional calculation represents a 4×4 configuration interaction which includes the ground state, the two singly excited states, ${}^2\Psi_{\pi\pi^*}^{1,3}$, and the selected doubly excited state. The numerical results with and without inclusion of the doubly excited configuration are collected in table 1. The change in the average configuration energy is roughly equal to the change in the HOMO-LUMO gap which can be understood by considering the Coulomb and exchange integrals of the $\pi^* \leftarrow \pi$ excitation in the various systems. Moderate mixing of the π and π^* levels subsequent to ionization yield $J_{\pi\pi^*}^{Z+1} > J_{\pi\pi^*}^N$. However, these changes are approximately compensated for by the concomitant relationship $K_{\pi\pi^*}^{Z+1} > K_{\pi\pi^*}^N$, and leads to an interpretation based on eqs. (2). Obviously the doubly excited configuration has only a moderate influence on the results of the gas phase molecule.

Calculation of the shake-up intensities is based on the relationship derived by Darko et al. [21] assuming only valence orbital overlap between initial and final state one-electron functions. The localization of the one-electron π and π^* orbitals subsequent to nitro group ionization is considerably different from those in the neutral molecule which gives rise to shake-up intensities of 23% for ${}^2\Psi_{\pi\pi^*}^1$ in the case of $\text{O } 1s$ ionization and 41% in the case of ${}^2\Psi_{\pi\pi^*}^1$ for an $\text{N } 1s$

ionization. The energies and intensities are relatively unchanged when the doubly excited configuration is included (see table 1). The triplet coupled doublet states have negligible intensity in the gas phase spectrum. Both ${}^2\Psi_{\pi\pi^*}^{1,3}$ ($\text{N } 1s$) final states are within ≈ 1.6 eV of the primary hole state and hence only contribute to the width of the signal while the computed ${}^2\Psi_{\pi\pi^*}^1$ ($\text{O } 1s$) intensity approximates the satellite structure in fig. 2.

The crystal structure of PNA [22] indicates that the molecules are arrayed in such a fashion that the

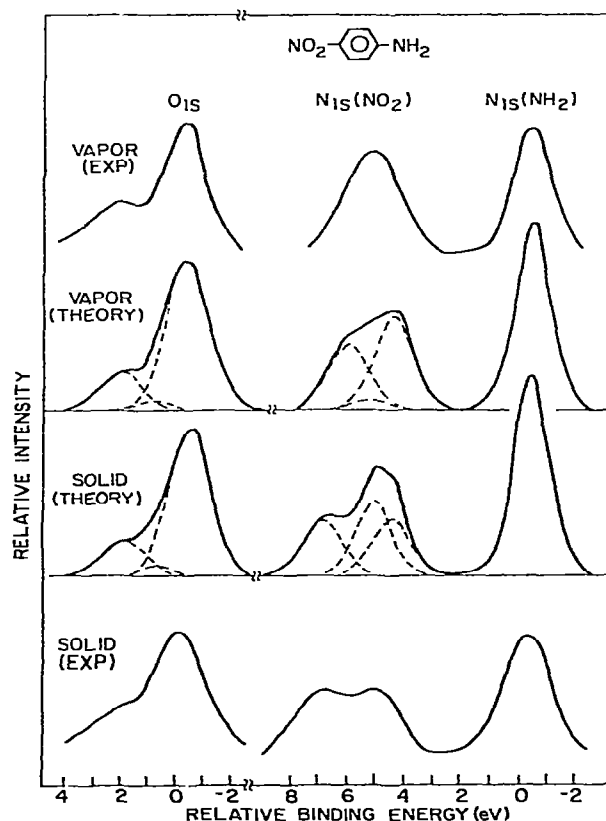


Fig. 2. A comparison of the vapor [6] and condensed phase [4,5] $\text{O } 1s$ and $\text{N } 1s$ (NO_2) XPS spectra of PNA with the equivalent-core results. The theoretical spectra are arbitrarily aligned with experiment to achieve the best agreement. Alignment of the $\text{N } 1s$ (NO_2) spectra is relative to the single $\text{N } 1s$ (NH_2) lines (binding energy = 0) [4-6]. Details of the mixing of ${}^2\Psi_{\pi\pi^*}^{1,3}$ with the primary hole state are given by Freund and Bigelow [15].

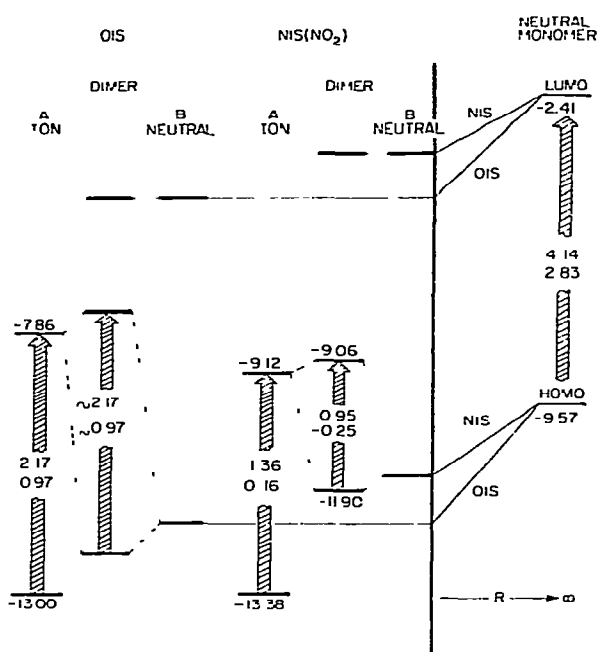


Fig. 3 A schematic representation of the gas to condensed phase orbital interactions (eV). Excitation energies between the indicated levels are (top and bottom, respectively) ${}^1\tilde{E}$ and ${}^3\tilde{E}$ for the neutral PNA monomer, and ${}^2\tilde{E}^1(k)$ and ${}^2\tilde{E}^3(k)$ for the ionic systems.

five nearest neighbors of each functional group are functional groups of opposite character, i.e. NO_2 groups are surrounded by NH_2 groups, and vice versa. We approximate such an environment by considering a series of dimers based on various pairing schemes of the crystal [7]. Fig. 3 gives an orbital scheme representing the coupling between an ionized molecule and its environment. We find that for an end-to-end pairing, for example, the N 1s (NO_2) core-hole induces significant intermolecular interaction: (1) mixing between the one-electron ionic monomer π^* level and the π level of the "neutral" portion results in a negative value for \tilde{E}_{av} as shown in fig. 3, (2) the intensities of ${}^2\Psi_{\pi\pi^*}^1$ and ${}^2\Psi_{\pi\pi^*}^3$ are $\approx 30\%$ (the latter being induced by the low-lying double excitation), and (3) intermolecular screening of the core-hole where $\approx 0.5 e$ of valence charge is drawn from the "neutral" monomer to the site of ionization. The pulling down of the dimer \tilde{E}_{av} (see fig. 3) relative to the corresponding free-ion value is the molecular counterpart of core-hole-

induced mixing of adsorbate (ionic monomer) and substrate ("neutral" monomer) states [17,23,24]. In our dimer model, however, the essential features of the coupling between ionic and host levels can be best elucidated in terms of perturbation equations [25,26]. The second-order correction to ϵ_{π}^N due to mixing between π_N and π_{Z+1}^* is,

$$\Delta\epsilon_{\pi}^N = (\epsilon_{\pi^*}^{Z+1} - \epsilon_{\pi}^N)^{-1}$$

$$\times |\langle \pi_{Z+1}^* | H' | \pi_N \rangle - \langle \pi_{Z+1}^* | \pi_N \rangle \epsilon_{\pi}^N|^2. \quad (5)$$

where $\langle \pi_{Z+1}^* | \pi_N \rangle = S_{\pi\pi^*}$ is the overlap matrix and $\langle \pi_{Z+1}^* | H' | \pi_N \rangle = H'_{\pi\pi^*}$ is the interaction matrix element between levels in the presence of the core-hole. Note that in fig. 3 we begin from the $Z+1$ levels fully relaxed in the presence of the core-hole with the neutral monomer removed to infinity. The orbital shifts indicated in fig. 3 as a function of R are approximations to the electrostatic first-order corrections, $\langle \pi_N | H' | \pi_N \rangle$, $H'_{\pi\pi^*}$ and ϵ_{π}^N are, therefore, functions of R to include variation in H' due to intermolecular charge rearrangement and $\langle \pi_N | H' | \pi_N \rangle$, respectively. $\Delta\epsilon_{\pi^*}^{Z+1}$ is given by interchanging the orbitals and eigenvalues.

In light of the approximations used the fact that our simple dimer model does not yield the experimental N 1s (NO_2) condensed phase shake-up intensity cannot be considered of serious consequence. It is easily rationalized that including a greater number of molecules in the simulation of the solid state could further reduce \tilde{E}_{av} . Also, delocalization of the orbitals implies increased intermolecular core-hole screening in the excited states and suggests that the approximation used to determine the free-ion multiplet splitting may not apply to extended structures ($K_{\pi k} \gg 0$ would serve to decrease $\Delta^2\tilde{E}_{\pi\pi^*}^{1,3}$).

SCF convergence difficulties prohibited explicit computation on O 1s dimer structures for reasonable values of R . However, eq. (5) and the free-ion eigenvalues given in fig. 3 serve to fully rationalize the experimental spectra. The O 1s core-hole, being closer to π_N , significantly increases $\langle \pi_N | H' | \pi_N \rangle$ compared to N 1s (NO_2) ionization and, therefore, the satellite structure is expected to be relatively unchanged on going from the vapor to the condensed phase.

In conclusion, we have shown that the vapor and condensed phase N 1s and O 1s XPS spectra of PNA can be rationalized on the basis of perturbations to the HOMO and LUMO π levels of the neutral free

molecule. In light of the strong mixing between states it appears a question of semantics as to how one characterizes the various peaks resolved in the core-hole spectra in terms of single configurations. Nevertheless, it is confirmed by our simple calculations that, particularly in the case of solid state N 1s (NO₂) ionization, the conditions for the existence of "negative shake-up" are fulfilled, although the term in itself may not be an appropriate choice.

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