# SHAKE-UP PHENOMENA IN D<sup>+</sup>--Ar--A<sup>-</sup> STRUCTURES: A CNDO/S EQUIVALENT-CORE STUDY ON N,N-DIMETHYL-*p*-NITROANILINE IN THE VAPOR AND CONDENSED PHASES

### Hans-Joachim FREUND\*

Physics Department, University of Pennsylvania, Philadephia, Pennsylvania 19104, USA

and

Richard W. BIGELOW

Xerox Webster Research Center, Webster, New York 14580, USA

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The nature and manifestations of perturbations to the valence orbital manifold of N,N-dimethyl-p-nitroaniline (DMPNA) in the vapor and condensed phases due to appropriate core-hole states are addressed within the equivalent-core approximation using the CNDO/S molecular orbital method. It is found that the doublet structures observed in the experimental solid phase XPS spectrum arising from N1s(NO<sub>2</sub>) and O1s ionization can be resolved in terms of intense shake-up excitations calculated to accompany creation of the appropriate core-hole. Furthermore, we find that the differences resolved in the gas and solid phase XPS spectra of p-nitroaniline, for example, for both O1s and N1s signals reflect both crystal polarization energies, and orbital mixing effects, and that modifications to the N1s(NO<sub>2</sub>) peak structure arising from the polar crystal environment are not inconsistent with an interpretation based on negative shake-up energies.

### 1. Introduction

Dipolar chemical species composed of aromatic chromophores parasubstituted with donor and acceptor groups  $(D^+-Ar-A^-)$  are a source of continuing interest from both an experimental and theoretical viewpoint. This appears the case particularly for the simple nitroanilines where recent studies have provided a more detailed assignment of excited states [1-6] in addition to addressing the nature of luminescence characteristics [7-9], intermolecular interactions [10] and the unusually large nonlinear second-order optical susceptibilities exhibited by these systems [11-14].

Of particular interest to us, however, is the unusually intense satellite structure accompanying heteroatom XPS core-level ionization reported for a series of  $D^+$ -Ar- $A^-$  structures in the solid state by Siegbahn and co-workers [15], and more recently by Pignataro,

On leave from: Lehrstuhl fur Theoretische Chemie der Universität zu Köln, 5000 Köln 41, West Germany.

Distegano and co-workers [16-19], and Tsuchiya and Seno [20]. The N1s(NO<sub>2</sub>) level of p-nitroaniline (PNA). for example, was shown to exhibit a characteristic doublet structure of approximately equal intensity  $(\Delta E \approx 1.8 \text{ eV})$  well separated from the apparently single component N1s(NH<sub>2</sub>) emission occurring at lower binding energy. Pignataro and Distefano [16] additionally resolved a relatively intense satellite  $\approx 2.4 \text{ eV}$ to the high binding energy side of the O1s peak. The early work of Siegbahn et al. [15] tentatively attributed such heteroatomic satellite features to radiation damage. Pignataro and Distefano [16], on the other hand, have discounted extrinsic mechanisms and interpret these characteristic satellites as inherent electronic processes, or shake-up transitions accompanying ejection of the appropriate core electron. Pignataro and Distefano exclude a mechanism involving radiation damage based on the observation that identical multipeak structures are resolved under varying experimental conditions, while hydrogen bonding effects were excluded due to the similarity between the results obtained for PNA

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and N,N-dimethyl-*p*-nitroaniline (DMPNA) [15,16] — the latter being a system well known not to support hydrogen bonding.

Based on many body-ab initio quantum chemical calculations on PNA Domcke and co-workers [21] assigned the high binding energy peak of the NIs(NO<sub>2</sub>) doublet to the primary core-hole, whereas the second lower energy peak was attributed to negative shakeup states arising from a superposition of singlet and triplet configurations of the D<sup>+</sup>-Ar-A<sup>-</sup> intramolecular  $\pi^* \leftarrow \pi$  charge-transfer excitations accompanying N1s(NO<sub>7</sub>) ionization - two-hole-one-particle states (2h1p). N1s(NH<sub>2</sub>) ionization, on the other hand, was shown to selectively destabilize these  $\pi^* \leftarrow \pi$  excitations which accounted for the absence of low energy shake-up structure associated with the donor nitrogen level. Although the computations yielded an intensity distribution and splitting of the  $Nls(NO_2)$ doublet structure in excellent correspondence with the experimental solid state data, the core-hole state of 1s and its accompanying satellite structure was not treated.

More recently Banna [22] reported gas phase XPS measurements on PNA<sup>‡</sup>. It was found that the O 1s spectrum was in good agreement with the solid phase results, whereas the nitrogen spectrum exhibited only the single components expected for the N1s(NO<sub>2</sub>) and N1s(NH<sub>2</sub>) primary core-holes (fig. 1). Based on the differences between the vapor and solid phase results, and the computations of Domcke et al. [21] where the assumed structure was that of a single unperturbed molecule (the gas phase environment), Banna concludes that. negative shake-up in PNA and structurally related systems (DMPNA, for example) has not been unambiguously demonstrated.

The purpose of this work is to show that the differences resolved in the gas and solid state spectra of PNA are the products of crystal polarization energies and that modifications to the N1s(NO<sub>2</sub>) peak structure in going to the condensed phase are not inconsistent with an interpretation based on negative shake-up energies.

In the following sections we present: (1) an outline of the theoretical methods we have elected to use and a discussion of their limitations; (2) a discussion of the neutral parent molecule and an outline of the intermolecular interactions perturbing the electronic structure in condensed media; (3) the results of cur computations

\* See note added in proof.

on the equivalent-core Z+1 free-molecule; (4) an extension of our treatment of intermolecular perturbations as applied to the core-hole molecules; and finally, (5) a summary of the conclusions which can be drawn based on our results.

2. Theoretical considerations of shake-up satellites and computational procedure

If it is assumed that during the course of ionization the ejected electron is not strongly correlated with the N-1 ionic system the probability for observing the  $N \rightarrow N-1$  event is given by [23,24],

$$P \simeq |\langle \phi_{\mathbf{e}} | A \cdot p | \phi_{\mathbf{h}} \rangle \langle \Psi_{\mathbf{F}}^{N-1} | a_{\mathbf{h}} | \Psi_{\mathbf{0}}^{N} \rangle |^{2} . \tag{1}$$

Assuming that  $\langle \phi_{\mathbf{e}} | \mathbf{A} \cdot \mathbf{p} | \phi_{\mathbf{h}} \rangle$  is constant for all final states the well known monopole-selection rule [24] is obtained,

$$P \propto |\langle \Psi_{N}^{N-1} | a_{h} | \Psi_{0}^{N} \rangle|^{2} , \qquad (2)$$

where  $|\Psi_{\rm F}^{N-1}\rangle$  is the final state of the ion and  $|\Psi_0^N\rangle$  is the ground state of the neutral molecule.  $a_{\rm h}$  is an annihilation operator which creates the core-hole in orbital  $|\phi_h\rangle$  leaving all other levels in  $|\Psi_0^N\rangle$  unchanged. In the experimental literature ionization peaks are usually defined in terms of main lines and satellites [25]. This distinction originates from the fact that the ionization probability to a final state  $|\Phi_{\rm F}^{N-1}\rangle$ , characterized by an orbital-ionization from a specific core level  $|\phi_{\rm h}\rangle$ (main line), is very often much larger than ionizations where, in addition to the core-level ionization, an electron is excited from the occupied to the unoccupied valence orbital manifold (shake-up transitions). Shakeup transitions usually lead to satellite structure on the high binding energy side of the main line due to the additional energy required to excite the valence electron. The intensity distribution between the main line and shake-up satellites reflects the quasi-particle nature of the outgoing electron. However, it has recently been demonstrated that, provided certain conditions are fulfilled, satellite features may appear on the low binding energy side of the most intense main line [26-28]. Such an ordering has been termed negative shake-up.

In order to define the energy contributions involved in these processes it is advantageous to compare excitations in the neutral molecule and in the ion. In terms of the closed shell neutral molecule an electronic excitation leads to singlet and triplet configurations with energies [29],

$${}^{1}E_{i \to j'} = \epsilon_{j'} - \epsilon_{i} - J_{ij'} + 2K_{ij'}$$
(3)

and

$${}^{3}E_{i \to j'} = \epsilon_{j'} - \epsilon_{i} - J_{ij'} , \qquad (4)$$

where  $\epsilon_{i(j')}$  are the orbital energies and  $J_{ij'}$  and  $K_{ij'}$ are the Coulomb and exchange integrals, respectively [29]. These excitations always lie above the ground state. Corresponding excitations in the presence of a core-hole ( $\epsilon_k$ ), however, lead to a somewhat more complex situation. Two doublet states and a quartet state may be formed by assuming various combinations of the three spins involved. Since an initially closedshell ground state is assumed only the doublet states can be populated by ionization in order to satisfy the spin selection rules. The energies of the two final doublet and the quartet configurations are given by [30]:

doublet I:

$${}^{2}E_{1}^{+} = -\epsilon_{i} - \epsilon_{k} + \epsilon_{j'} + J_{ik} - J_{j'k} - J_{ij'}$$

$$+ K_{ik} + \frac{1}{2}K_{ij'} + \frac{1}{2}K_{j'k}, \qquad (5)$$

doublet II:

$${}^{2}E_{2}^{+}=-\epsilon_{i}-\epsilon_{k}+\epsilon_{j'}+J_{ik}-J_{j'k}-J_{ij'}$$
  
- $K_{ik}+\frac{3}{2}K_{ij'}+\frac{3}{2}K_{j'k},$  (6)

quartet:

$${}^{4}E^{+} = -\epsilon_{i} - \epsilon_{k} + \epsilon_{j} + J_{ik} - J_{j'k} - J_{ij'} - K_{ik} , \qquad (7)$$

where the energy of the ground state has been set equal to zero. The splitting between doublet states  ${}^{2}E_{1}^{+}$  and  ${}^{2}E_{2}^{+}$  is,

$$\Delta^2 E_{1,2}^+ = {}^2 E_1^+ - {}^2 E_2^+ = 2K_{ik} - K_{ij'} - K_{j'k} .$$
(8)

Relating  ${}^{2}E_{1}^{+}$ , for example, to the corresponding neutral molecule excitation gives,

$${}^{2}E_{1}^{+} = -\epsilon_{k} + {}^{1}E_{i \to j'} + J_{ik} - J_{j'k} + K_{ik} + \frac{1}{2}K_{j'k} - \frac{3}{2}K_{ij'}.$$
(9)

Therefore, to achieve a state characterized by negative shake-up  $({}^{2}E_{1}^{+} \leq -e_{k})$  the following condition must be fulfilled [27,28]

$${}^{1}E_{i \to j'} \approx -(J_{ik} - J_{j'k} + K_{ik} + \frac{1}{2}K_{j'k} - \frac{3}{2}K_{ij'}).$$
(10)

Assuming for the present purposes that  $K_{ik}$ ,  $K_{j'k}$  and  $K_{ij'}$  are negligible relative to the Coulomb terms, and further assuming a common aromatic neutral molecule excitation energy of  $\approx 3-4$  eV, eq. (10) can only be satisfied for  $J_{j'k} \gg J_{ik}$ . Such a case arises whenever  ${}^{1}E_{i \rightarrow j'}$  involves a considerable transfer of charge between spatially distant regions, and  $|\phi_{h}\rangle$  and  $|\phi_{j'}\rangle$  are localized on the same portion of the molecule.  $J_{ik}$  and  $J_{i'k}$  are given as.

$$J_{ik} = \langle \phi_i(1)\phi_k(2)|1/r_{12}|\phi_i(1)\phi_k(2)\rangle$$
(11)

and

$$J_{j'k} = \langle \phi_{j'}(1) \phi_k(2) | 1/r_{12} | \phi_{j'}(1) \phi_k(2) \rangle, \qquad (12)$$

and serve to rationalize this statement. A schematic representation of the wavefunctions involved and the appropriate interactions are given in fig. 2. It is clear that  $J_{j'k}$  will be large relative to  $J_{ik}$  simply because the core-hole is created in a region of the molecule where the electron density of the electron donor orbital is small (as will be shown the situation outlined is similar to the one found in PNA and/or DMPNA).

Thus far the discussion has been limited to configuration energies connected with single determinant wavefunctions created from the Hartree—Fock determinant. In order to properly describe a spectroscopic state, configuration interaction must be considered which may alter the energy sequencing of states given by the pure configuration energies. In other words, if the configuration energies suggest negative shake-up, configuration interaction may lead to a situation where the states are so strongly mixed that an assignment in terms of *main* line and satellite components becomes a question of semantics [28].

Having illustrated the energetics of the shake-up process it is now appropriate to discuss the intensities more explicitly with particular emphasis on *probable* relative strengths of the multiplet components derived from the same spatial part of the wavefunction. For the three-spin case the following basis functions are used [30]:

aaa

Ιααβλ Ιαβαλ Ιβααλ

|ββα> |βαβ> |αββ>

(13)

(14)

(15)

which lead to the spin eigenfunctions,  $S_Z = \frac{3}{2}$  (Quartet):  $|\alpha\alpha\alpha\rangle$   $3^{-1/2} \{|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle\}$   $3^{-1/2} \{|\beta\beta\alpha\rangle + |\beta\alpha\beta\rangle + |\alpha\beta\beta\rangle\}$   $|\beta\beta\beta\rangle$ ,  $S_Z = \frac{1}{2}$  (Doublet I):  $2^{-1/2} \{|\alpha\beta\alpha\rangle - |\alpha\alpha\beta\}\}$  $2^{-1/2} \{|\beta\alpha\beta\rangle - |\beta\beta\alpha\rangle\}$ ,

 $S_{Z} = \frac{1}{2} \text{ (Doublet II):}$   $6^{-1/2} \{2|\beta\alpha\alpha\rangle - |\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle\}$   $6^{-1/2} \{2|\alpha\beta\beta\rangle - |\beta\alpha\beta\rangle - |\beta\beta\alpha\rangle\}.$ (16)

Referring to the excitations in the neutral system the doublet-I state may be viewed as the singlet-coupled-doublet state, whereas the doublet II-state is a spin-polarized state and may be termed the triplet-coupled-doublet state [31]. According to eqs. (5) and (6)  ${}^{2}E_{2}^{+} < {}^{2}E_{1}^{+}$ . Fig. 3 indicates the parantage relationship in the form of a branching diagram.

There are two options available to express the total wavefunction of the multiplets with respect to the spatial part of the wavefunction: (1) the basis orbitals  $|\phi_i\rangle$  of the neutral system  $|\Phi_{(1)}^N\rangle$ ; and, (2) the basis orbitals  $|\chi_i\rangle$  of a self-consistantly calculated one-determinantal ion state  $|\Phi_{IS}^{N-1}\rangle$ . If option (1) is selected the number of configurations to be considered may be large, whereas beginning from option (2) only a few configurations may be sufficient to adequately describe the system. We have, therefore, elected the latter course and begin from a self-consistently calculated hole-state where the hole is localized to partially account for the final state correlation [32-34]. The excited states of the ion are then calculated in terms of these basis orbitals applying the usual configuration interaction procedure. Assuming for simplicity that each of the final multiplet states can be described in terms of a single singly-excited configuration, the singlet and tripletcoupled doublet states are,

$$2\Psi_{\rm F}^{1} = d_0 |\Phi_{\rm IS}^{N-1}\rangle |\alpha\rangle + d_{ij}a_i a_j^+ |\Phi_{\rm IS}^{N-1}\rangle \times \{2^{-1/2} (i\alpha\beta\alpha) - i\alpha\alpha\beta)\}$$
(17)

and

$$|^{2}\Psi_{\rm F}^{2}\rangle = d_{0}|\Phi_{\rm IS}^{N-1}\rangle|\alpha\rangle + d_{ij}a_{i}a_{j}^{\dagger}|\Phi_{\rm IS}^{N-1}\rangle \\ \times \{6^{-1/2}(2|\beta\alpha\alpha\rangle - |\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle)\}.$$
(18)

In terms of eq. (2) the relative intensities are then given by

$${}^{2}P_{1} \propto [d_{0} \langle \Phi_{\text{IS}}^{N-1} | a_{\text{h}} | \Phi_{0}^{N} \rangle + 2^{1/2} d_{ij} \langle a_{i} a_{j}^{+} \Phi_{\text{IS}}^{N-1} | a_{\text{h}} | \Phi_{0}^{N} \rangle]^{2}, \qquad (19)$$

and

$${}^{2}P_{2} \alpha |d_{0}^{\prime} \langle \Phi_{\mathrm{IS}}^{N-1} | a_{\mathrm{h}} | \Phi_{0}^{N} \rangle |^{2} .$$
<sup>(20)</sup>

Eqs. (19) and (20) emphasize that the singlet and triplet-coupled doublet state intensities are generally unequal. Provided that the orbitals of the N-1 system which are not primary contributors to ionization and/ or excitation essentially retain their neutral state charac-



Fig. 1. A reconstruction of the O1s and N1s XPS vapor [22] and condensed phase [15,16] spectra of *p*-nitroaniline. The peak maxima of the O1s and N1s (amino) signals are arbitrarily aligned at zero binding energy. Siegbahm et al. [15] and Pignataro and Distefano [16] resolve an entirely equivalent XPS powder spectrum for N,N-dimethyl-p-nitroaniline.

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Fig. 2. A schematic representation of the energy levels and wavefunctions leading to shake-up characterized by chargetransfer.

ter the following approximations are valid:

$$\langle a_i a_j^{\dagger} \Phi_{\rm IS}^{N-1} | a_h | \Phi_0^N \rangle \approx \langle \chi_j | \phi_i \rangle \tag{21}$$

and

$$\langle \Phi_{\rm IS}^{N-1} | a_{\rm h} | \Phi_0^N \rangle \approx 1 .$$
 (22)

Subject to these conditions eqs. (19) and (20) reduce to,

$${}^{2}P_{1} \propto |d_{0} + 2^{1/2} d_{ij} \langle \chi_{j} | \phi_{i} \rangle |^{2} .$$
<sup>(23)</sup>

and

$${}^{2}P_{2} \propto |d_{0}'|^{2}$$
 (24)

 ${}^{2}P_{1}$  and  ${}^{2}P_{2}$  further reduce to the expressions of Darko et al. [31] for  $d_{ij} \ge d_{0}$ . Although the approximations given by eqs. (21) and (22) may not be justified under all conditions, eqs. (23) and (24) suggest that as a *rule-of-thumb* the intensity of the singlet-coupled doublet state is greater than that of the triplet-coupled doublet. There is both experimental and theoretical evidence supporting this conclusion [28,35,36].

The ground and excited states of the neutral molecule and the appropriate ions are obtained using the closed-shell all-valence-electron spectroscopic CNDO/S program of Del Bene and Jaffe [37-39] as developed by Ellis et al. [40]. The program was used as obtained from QCPE [41]. In the framework of this method it is not possible to calculate proper doublet core-hole states since the core electrons are not explicitly taken into consideration. Nevertheless, it has been shown by several workers [34,42-44] that a localized core-hole



Fig. 3. A branching diagram indicating the multiplicity of the states which can be constructed from the indicated number of nonequivalent electrons. Also indicated is the electronic structure of the states of current interest. The excitations characterized as singlet and triplet are referred to the closed-shell (Z+1)-ground state parantage, and are the singlet and triplet-coupled doublet states of the ion, respectively.

state can be successfully simulated by using an equivalent-core approximation. This is accomplished by replacing the atom to be ionized (atomic number Z) by the atom following in the periodic table (atomic number Z' = Z + i) and calculating the system as a cation. This system can be treated within a closed-shell formalism although the influence of the core-hole on the valence electrons is simulated. The excitations described by a configuration interaction treatment are obtained by accounting for potential changes and should, therefore, resemble excitations in the actual ionic system. However, excitations in the (Z+1)-system are classified according to singlet and triplet character and, consequently, do not directly correspond to the doublet final states of interest. A comparison can nevertheless be achieved by assuming that the change in



Fig. 4. An energy level diagram demonstrating the relationship of the singlet and triplet states of the closed-shell (Z+1)-ground state to the average configuration energy and the excitations in the ion having corresponding valence orbital character.

average configuration energy calculated from the (Z+1)-system is reasonably described. Since the splitting of the multiplets relative to the average configuration energy is contained in eqs. (5)-(7) the appropriate multiplet energies can be determined provided the approximate electron-core-hole exchange interaction is known. Fig. 4 gives a schematic indication of the levels of interest and their relative spacings. Since it is desired to apply such a reasoning to a specific system a knowledge of the particular one-electron orbital forms enable an extraction of the appropriate splitting. It is well known that exchange interactions are related to the overlap of the one-electron wavefunctions. From fig. 2 it is easily verified that  $K_{ik}$  and  $K_{ii} \approx 0$ , while  $K_{i'k}$ may be relatively large and thus determine the splitting. To a first-order approximation  $K_{i'k}$  is an exchange interaction between an atomic 1s-orbital and  $\pi$ -orbital component of the LUMO level (see discussion below),

$$K_{j'k} = \langle \phi_{1s}(1)\phi_{\pi}^{\text{LUMO}}(2) | 1/r_{12} | \phi_{1s}(2)\phi_{\pi}^{\text{LUMO}}(1) \rangle .$$
(25)

In accordance with this simple argument one of the two doublet final state energies is given by the average configuration energy of the (Z+1)-system and the

other by this energy increased by  $K_{i'k}$ ,

$${}^{2}E_{1}^{+}=E_{avg}^{-}$$
, (26)

and

$${}^{2}E_{2}^{+} = E_{avg} + K_{i'k} . (27)$$

In order to apply eqs. (23) and (24) to the study of shake-up intensities  $d_0$  and  $d'_0$  must, of course, be known. However, in accord with Brillouin's theorem [45],  $d_0$  and  $d'_0$  can only be extracted from a configuration expansion based on Hartree-Fock orbitals if at least double excited configurations are included. Since the present version of the CNDO/S method has been specifically parameterized to describe molecular excited states based on singly excited configurations we elect to approximate the interactions between the ground and higher-lying states by considering the simple 4 X 4 configurational interaction problem as structured in fig. 5. The diagonal elements correspond to the configuration energies relative to the ground state. Although the configuration energy for arbitrary double excited states can be easily determined provided the appropriate orbitals are defined, we restrict our treatment to the two-state system of fig. 5. The double excitation energy



Fig. 5. A schematic representation of the  $4 \times 4$  configurational interaction problem used to indirectly couple the CNDO/S equivalent-core singly-excited singlet (SSES) and triplet (TSES)coupled doublet states with the core-hole (GS) through interaction with the indicated double excited configuration.

in this case is given simply by,

$${}^{D}E_{i\to j'} = 2\Delta\epsilon_{ij'} + J_{ii} + J_{j'j'} - 4J_{ij'} + 2K_{ij'} .$$
(28)

In addition, instead of explicitly calculating the offdiagonal matrix elements, given for example by Cizek [46], we choose to merely examine the qualitative features of the indirect coupling by treating these elements as parameters equal to 1.0 eV. The singly excited singlet and triplet-coupled doublet configuration energies (SSES and TSES, respectively) are taken from the CNDO/S (Z+1)-system results adjusted in accord with the above arguments.

It now remains to apply this general treatment to the specific case of the DMPNA/PNA structures. Domcke et al. [21,47] used the above rationalizations based on the relative localization of the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals to show that these molecules are candidates for negative shake-up structure. As can be seen from fig. 6, for example, the HOMO level of DMPNA is localized mainly on the amino substituent while the LUMO level is localized on the nitro group. Therefore, any shake-up derived from an excitation between these orbitals will be accompanied by a considerable charge-transfer from the amino to the nitro group. Thus, a N1s-hole created on the nitrogen of the NO<sub>2</sub>-group will be effectively screened by coupling to this transition while for a N1s-hole on the nitrogen of the amino group the opposite is the case. Translating this result into electron-hole interactions; in the former case  $J_{j'k} \gg J_{ik}$  while  $J_{ik}$  $\gg J_{j'k}$  in the latter case. This means that a N1s-hole on the NO<sub>2</sub>-group leads to a situation where negative shake-up is possible while such a situation can be excluded for the N(CH<sub>3</sub>)<sub>2</sub>-group. Oxygen ionization which occurs on the NO<sub>2</sub>-group is of course a candidate for negative shake-up peaks in the same sense as N1s (NO<sub>2</sub>) ionization.

The above discussion based on electron-hole interactions is limited to electron configurations. The energies of the spectroscopic states, however, are additionally dependent on configuration interaction. Although the energies of the calculated shake-up peaks will be somewhat modified due to configuration interaction, it is expected that the generally different behaviour of shake-up derived from ionizations from the  $N(CH_3)_2$ and NO<sub>2</sub>-groups will be preserved. Following the scheme outlined in this section the only additional parameter that must be included is the exchange splitting  $K_{ik}$ given by eq. (25). It is expected that the experimentally observed splitting of the N1s-ionization in the free NO molecule (1.2 eV) [48] is a reasonable approximation to this quantity since this splitting is basically determined by the exchange between an atomic core 1s-level and a  $2p-\pi$  molecular orbital.

Intramolecular atomic coordinates are based on the bond lengths and bond angles given by Pople and Beveridge [49] rather than the more commonly used crystalographic data of Mak and Trotter [50]. It is our experience that coordinate differences resulting from the two sets of values do not lead to significant differences in the properties of current interest. Also our work deals primarily with DMPNA, although reference is made throughout to computational results on selected PNA supermolecule (dimer) configurations. We find this course convenient since computations on the former species had been carried out prior to the vapor phase XPS results of Banna [22]. It was not considered necessary to duplicate the effort for PNA as the effect of methyl group substitution on the donor nitrogen is expected to be of little consequence for the present purposes.



Fig. 6. The CNDO/S energy and orbital forms (as viewed from above the molecular plane) of selected occupied and virtual levels of neutral DMPNA. The relative magnitudes of the orbital lobes are drawn proportional to the atomic orbital coefficients. Only the carbon and heteroatom framework is given. The hydrogen centers attached to the benzene moeiety have significant density in the 12a'( $\sigma$ ) orbital, whereas the methyl hydrogens have a non-negligible density in the 17a'( $\pi$ ) orbital.

The CNDO/S-CI program, as written, provides for the choice of several approximations to the two-center Coulomb repulsion integrals,  $\Gamma_{AB}$ : the most common of which are the Pariser—Parr [51,52] and Nishimoto— Mataga [53] integrals. It has been suggested in the literature, with particular emphasis on benzene-derived systems, that when these integrals are used with the CNDO/S parameterization the Nishimoto—Mataga integrals yield better singlet states while the Pariser—Parr approximation is better suited for triplet states [54– 56]. Where appropriate the results using both methods are discussed. Most importantly, however, we find that *average* configuration energies derived from the various (Z+1)-system excitations of interest are to a good approximation independent of the method used to evaluate  $\Gamma_{AB}$ .

Excited states for the neutral and closed-shell (Z+1)systems are generated from the CNDO/S ground state occupied and virtual orbitals through a configuration interaction procedure among the 60 lowest energy oneelectron excitations. It is these states of the (Z+1)system which are adjusted in the above described manner to properly reflect the ionic electronic structure.

### 3. The DMPNA neutral state

Prior to addressing the relevant core-level ion states of DMPNA (PNA) it is advantageous to provide a firm foundation for later comparisons by establishing the nature of various interactions within the valence orbital manifold of the neutral species in the vapor and condensed phases. Fig. 6, therefore, compares the eigenvalues of selected virtual and occupied levels of DMPNA together with a schematic representation of the corresponding wavefunctions. Table 1 presents the eleven lowest energy singlet and three lowest energy triplet one-electron excitations arising from appropriate combinations of the orbitals given in fig. 6. Although there appears to be some controversy concerning the precise number of transitions occurring in the low energy spectral region [3,6], the relative polarizations appear to be well characterized [3,6] and in approximate accord with the ordering of states in table 1. Particularly, the lower-energy strongly allowed transitions yield a theoretical  $S_n \leftarrow S_0$  excitation spectrum in excellent correspondence with the experimental gas phase absorption of PNA [3,6]. Although DMPNA has not received the experimental attention of PNA it is expected that the character of these excited states is similar. Since excitations involving strongly allowed intramolecular chargetransfer states are of primary interest an incorrect sequence of excitations of lesser intensity cannot be considered of serious consequence. It should be noted, however, that while Khalik and co-workers [6] suggest that the low energy  $\pi^* \leftarrow n$  singlet states obtained by the CNDO/S-CI method are artifacts of the MO scheme other workers using different techniques argue for their presence [3]. Based on solvent shifts analyses [57] and numerous additional molecular orbital computations [3,6,9,11,12,58] the intensity in the 4-5 eV gas phase

### Table 1

The CNDO/S-Cl lower-lying singlet and triplet transitions of DMPNA. Included is the transition character ( $C_s$  symmetry), excitation energy (eV), oscillator strength (f), polarization [long (t) and short ( $\leftrightarrow$ ) axis, respectively],  $E_{sol}(eV)$  (relative to the ground state) where  $E_{sol} = k_e E'_{sol}$  with  $k_e = \frac{1}{2} (1 - e_D^{-1})$  as described in the text,  $\mu^{*}(\theta = 30^{\circ})$  (debye), and the two leading one-electron Cl elements of the wavefunction. In our version of CNDO/S excited state dipole moments are only computed for levels  $^{1,3}E_n$  whose  $^{1,3}E_n + ^{1,3}E_1$  oscillator strength was >10<sup>-4</sup>, a condition which is not achieved for the excitations of interest. We have, therefore, included the excited state dipole moments of interest from a DMPNA configuration where the nitro-group was twisted 30° out of the ring plane  $-\mu_g = 8.08$  D. Dipole moments for the two lowest singlets and lowest triplet are undoubtedly too large due to a slight mixing with the charge-transfer state

Transition	Energy	f	Polari- zation	E'sol	$\mu^*(\theta=30^\circ)$	Wavefunction
Singlets						
$1^{1}A^{n}(\pi^{*}\leftarrow n)$	2.97		**	-2.80	<7.65	$-0.841 \oplus (27 \rightarrow 33) + 0.375 \oplus (28 \rightarrow 33) +$
$2^{1}A'(\pi^{*} \leftarrow n)$	3.05	$5.0 \times 10^{-5}$	+ \$	-2.54	<9.50	$0.905 \oplus (25 \rightarrow 33) + 0.342 \oplus (26 \rightarrow 35) +$
$3^1 A'(\pi^* \leftarrow \pi)$	4.14	0.59717	<b>‡</b>	4.68	19.62	$-0.976 \oplus (32 \rightarrow 33) - 0.148 \oplus (29 \rightarrow 33) +$
4 <sup>1</sup> A"(π*←π)	4.41	0.00024	**	1.98		0.749φ (31→ 33) – 0.604φ (32 → 34) +
$5^{1}A''(\pi^{*}\leftarrow\pi)$	5.26	0.10500	<b>4</b> *	1.12		0.654¢ (31→33) + 0.685¢ (32→34)+
$6^1 A'(\pi^* \leftarrow \pi)$	5.81	0.01082	<b>‡</b>	0.00		$-0.911 \phi (32 \rightarrow 35) + 0.289 \phi (31 \rightarrow 34) +$
7 <sup>1</sup> A"(π*+-π)	5.97		<b>+</b> +	1.60		$-0.841 \oplus (28 \rightarrow 33) - 0.352 \oplus (27 \rightarrow 33) +$
8 <sup>1</sup> A″(π*←π)	6.37	0.10780	**	-3.82		$-0.882 \oplus (30 \rightarrow 33) - 0.450 \oplus (31 \rightarrow 35) +$
$9^{1}A'(\pi^{*} \leftarrow n, \pi)$	6.53	0.11163	\$	-0.50		$-0.860 \oplus (28 \rightarrow 34) - 0.349 \oplus (31 \rightarrow 34) +$
$10^{1} A'(\pi^* \leftarrow \pi, n)$	6.59	0.63077	ŧ	-0.32		-0.838 ¢ (31 → 34) + 0.355 ¢ (28 → 34) +
11 <sup>1</sup> A″(π*← π)	6.71	0.75351	**	-1.22		$0.761 \oplus (31 \rightarrow 35) - 0.429 \oplus (30 \rightarrow 33) +$
Triplets						
$1^{3}A''(\pi^{*} \leftarrow \pi)$	1.78		÷	-4.22	<5.69	-0.928¢ (30→33) -0.356¢ (30→35) +
$2^{3}A'(\pi^{*} + \pi)$	2.83		\$	2.80	16.73	$-0.802 \oplus (32 \rightarrow 33) \pm 0.367 \oplus (32 \rightarrow 35) \pm$
$3^{3}A''(\pi^* \leftarrow \pi, \pi)$	2.97		•++	2.80	-	$0.841 \oplus (27 \rightarrow 33) - 0.375 \oplus (28 \rightarrow 33) +$

absorption spectrum has been well characterized as due primarily to excited state charge-transfer from the amino (donor) nitrogen to the nitro (acceptor) fragment – the  $3 {}^{1}A'(\pi^{*} \leftarrow \pi)$  excitation of table 1. In addition, fluorescence and phosphorescence measurements on DMPNA in EPA glass yield a considerably smaller  ${}^{1}E_{CT} - {}^{3}E_{1}$  separation ( $\approx 0.5 \text{ eV}$ ) [9] than given in table 1 (2.36 eV). As noted in the previous section the computed  ${}^{1}E_{CT} - {}^{3}E_{1}$  separation can be improved upon using Pariser-Parr integrals ( $\Delta E = 1.1$ eV relative to  ${}^{1}E_{CT}$  of table 1). As will become evident from the following discussion electrostatic solvent effects will further decrease this splitting. Also using the CNDO/S-CI method Carsey et al. [9] apparently obtain an  ${}^{3}E_{1}$  state characterized by a large  ${}^{3}\Phi(32 \rightarrow$ 33) component - the second lowest-lying triplet in table 1. Although the reason for this discrepancy is unclear, it is pointed out by Carsey and co-workers [9] that the luminescence properties only exclude  $\pi^* \leftarrow n$  contributions to  ${}^{3}E_{1}$ . Domcke et al. [21] calculate a singlet and triplet-coupled doublet state separation for PNA of  $\approx 0.5$  eV; however, their neutral molecule excitation energies (configuration energies) were several eV higher than experiment ( ${}^{3}E_{1} \approx 6.09$ eV).

Neutral DMPNA (PNA) has a relatively polar ground state structure (D<sup>+</sup>-Ar-A<sup>-</sup>) as shown in fig. 7 where the dipole moment ( $\mu_g$ ) is directed along the long molecular axis. In terms of conventional macroscopic solvent reaction field theory [57,59] a non-zero ground state dipole moment implies that the solute molecule is stabilized in polar fluid media due to selective orientation of solvent sites – i.e. negative/positive centers of the polar solvent can be viewed as preferentially drawn toward the positive/negative regions of the solute molecule. This selective distribution of solvent charge centers about the solute system (characterized by an appropriate cavity parameter) acts back on the solute with a field strength.

$$\mathcal{E}_{\mathrm{R}} = \mu_{\mathrm{g}} f(\epsilon_{\mathrm{D}}, \alpha) , \qquad (29)$$

where  $f(e_D, a)$  is a function of the media dielectric con-



Fig. 7. The CNDO/S ground state  $\sigma + \pi$  and  $\pi$  (enclosed) atomic charge densities of neutral DMPNA. Brackets denote corresponding values for the indicated regions of the system (negative values denote an excess charge). The hatched areas represent the selective induction of net charge in the surrounding space when DMPNA is imbedded in a dielectric medium.

stant  $\epsilon_D$  and solute cavity radius *a*. Since we will be mainly interested in first-order electrostatic effects polarizability and dispersion contributions, for example [59], are excluded from the following discussion. Within the present framework the solvation energy, or net stabilization energy of the ground state due to electrostatic solvent/solute interaction is given by,

$$\Delta E_{g}^{ES} = -\mu_{g} \mathcal{E}_{R} , \qquad (30)$$

or, in terms of 
$$\mu_{g}$$
,

$$\Delta E_{\Sigma}^{\text{ES}} = -\mu_{\text{g}}^2 f(\epsilon_{\text{D}}, a) \,. \tag{31}$$

Provided the solvent does not reorient upon excitation an excited state of dipole moment  $\mu_e$  is stabilized by,

$$\Delta E_{\rm e}^{\rm ES} = -\mu_{\rm e} \,\mu_{\rm g} \, f(\epsilon_{\rm D}, a) \,. \tag{32}$$

Eq. (32) characterizes the non-relaxed state and corresponds to the structure commonly probed by absorption measurements  $-\mu_e > \mu_g$  implies a red-shift in excitation energy as the solvent dielectric constant is increased. In the case where the solvent does reorient in response to  $\mu_e > \mu_g$  a reaction field

$$\mathcal{E}_{\mathrm{R}} = \mu_{\mathrm{e}} f(\epsilon_{\mathrm{D}}, a) \,, \tag{33}$$

leads to additional stabilization.

$$\Delta E_{e'}^{\text{ES}} = -\mu_e^2 f(\epsilon_{\text{D}}, a) , \qquad (34)$$

characterizing the structure commonly probed by fluorescence techniques. Therefore, in polar fluid media the  $3^{1}A'(\pi^{*} \leftarrow \pi)$  excitation of neutral DMPNA is shifted to lower energy relative to the gas phase. Using eqs. (31)-(34) Ledger and Suppan [57] obtain  $\mu_{e} = 16.3$ and 14.0 debye for the  $E(\Phi_{CT})$  state of PNA from absorption and fluorescence measurements, respectively, based on an experimental  $\mu_{g} = 6.0$  debye ( $\mu_{g} = 8.35$  B according to the present CNDO/S results). Furthermore, Ledger and Suppan [57] find that in the most polar solvents  $E(\Phi_{CT})$  is stabilized by  $\approx 1.0$  eV relative to the gas phase.

The alternative approach to solvent/solute interaction due to Jano [60] has been programmed and included in the CNDO/S-CI package. Jano considers the solvation energy  $E_{sol}$  proportional to the *self-energy* of the solute electronic charge distribution modified by a dielectric screening term. In terms of one-electron wavefunctions and the LCAO approximation Jano obtains,

$$-E_{\text{sol}} \approx k_{e} \left[ \sum_{A} Q_{A}^{2} \Gamma_{AA} + 2 \sum_{A \neq B} Q_{A} Q_{B} \Gamma_{AB} \right], \quad (35)$$

where  $k_e = \frac{1}{2}(1 - \epsilon_D^{-1})$ ,  $Q_A$  and  $Q_B$  are atomic charges, and  $\Gamma_{AA}$  and  $\Gamma_{AB}$  are appropriate approximations to the one- and two-center Coulomb integrals. For excited states eq. (35) describes the *relaxed* solvent/solute configuration. As  $\epsilon_D \rightarrow \infty$  eq. (35) yields a red-shift in the  $3^1A'(\pi^* \leftarrow \pi)$  transition energy relative to the freemolecule of 2.34 eV (table 1) which is approximately a factor of two too large. In addition, an  $E_{sol} = 2.38$ eV ( $\epsilon_D \rightarrow \infty$ ) calculated for the DMPNA ground state approaches the values commonly obtained for ion solvation [59,60]. Although eq. (35) does not appear to have been systematically applied to solvent shifts, and, therefore, no standard for accuracy in this regard is



Fig. 8. A schematic representation of the LUMO and HOMO levels of neutral DMPNA and the DMPNA/NH<sup>+</sup> supermolecule as viewed from above the molecular plane. The atomic orbital coefficients comprising the molecular orbitals are given opposite the appropriate center. Also given are the orbital shifts responsible for the  $\Phi_{CT}$  red-shift in going from the unperturbed to the supermolecule system. The free molecule static perturbed values were obtained in accordance with eq. (39) assuming  $Q_C = +1.0e$  located equivalent to the N(NH<sup>+</sup><sub>4</sub>) position in the supermolecule and  $f_{AC}(R) = R_{AC}^{-1}$ . The smaller shift obtained for the supermolecule relative to the static perturbed system appears due to the difference in the variation of the two-center Coulomb integral as a function of separation rather than polarization effects.

available, the source of these rather large discrepancies can be attributed to the overestimation of the net atomic charges as reflected by the difference between the experimental and calculated ground state dipole moments. It should also be noted that recent studies raise considerable question as to the appropriate  $k_e$ term to describe solvent/solute interaction [63]. However, it suffices here merely to emphasize that eq. (35) derived from a consideration of electrostatic solvent/ solute interaction can be used as a measure of the direction and approximate relative magnitude of shifts in the neutral molecule excited states as a function of solvent polarity.

Although eqs. (29)-(35) offer a qualitative indication of solvent effects, it is instructive to also approach these intermolecular effects in terms which directly reveal the orbital nature of the interaction. Klopman [64], Germer [65,66], Miertuš and Kysel [61], and Constanciel and Tapia [63] have approximated solvent effects within a MO framework by envisioning solvatons of charge  $Q_{A'} = -Q_A$  associated with each atomic center. Interactions between  $Q_{A'}$  and the electrons of the free-molecule are included directly in the SCF energy minimization procedure by adding a coulombic term of the form,

$$V_{\mu\mu} = -k_{\rm e} \left[ Q_{\rm A'} \Gamma'_{\rm AA}(R) + \sum_{\rm B\neq A} Q_{\rm B'} \Gamma'_{\rm AB}(R) \right], \quad (36)$$

to the diagonal elements of the Fock operator.  $k_e$  is again a screening constant which depends on the medium dielectric constant, and  $\Gamma'_{AA}(R)$  and  $\Gamma'_{AB}(R)$  are modified one- and two-center Coulomb terms, respectively. Rendering these interactions in terms of first-order perturbation theory one obtains the change in binding



Fig. 9. The truncated intermolecular pairing scheme used to approximate the PNA crystal structure. The three planes define selected trimer configurations.

energy of molecular orbital  $|\phi_i\rangle$  due to interaction with a static external charge center [67]

$$\Delta \epsilon_i = \langle \phi_i | H' | \phi_i \rangle \,. \tag{37}$$

The LCAO approximation reduces eq. (37) to,

$$\Delta \epsilon_i = \sum_{A} c_{iA}^2 \langle \varphi_A | H' | \varphi_A \rangle, \qquad (38)$$

where  $c_{iA}$  is the AO coefficient of atomic orbital  $|\varphi_A\rangle$ . Approximating H' as a coulombic interaction between a non-overlapping point charge and the atomic charges the displacement of  $|\phi_r\rangle$  is given in eV by,

$$\Delta \epsilon_{i} = 14.38 \sum_{A} \sum_{C} c_{iA}^{2} [Q_{C} f_{AC}(R)] , \qquad (39)$$

where  $f_{AC}(R)$  contains the appropriate distance dependence in angstroms and  $Q_C = \pm \delta e$ . An entirely equivalent expression can be obtained from the solvation model [62].

Qualitatively the negative charge opposite the DMPNA (PNA) amino nitrogen in polar media (fig. 7) will destabilize the HOMO more than the LUMO which is localized at the opposing end of the molecule, while concomitantly the positive charge opposite the nitro group will stabilize the LUMO more than the HOMO. Such selective orbital perturbation produces the red-shift in the  $3^{1}A'(\pi^{*} \leftarrow \pi)\Phi_{CT}$  excitation predicted by macroscopic theories.

We have simulated an electrostatic interaction scheme by placing NH<sub>4</sub><sup>+</sup> opposite the nitro fragment of DMPNA and performing a supermolecule SCF calculation –  $R[N(NO_2)-N(NH_4^+)] = 4.0$  Å. Fig. 8 shows that the computed red-shift in the  $\Phi_{CT}$  excitation is in qualitative accord with perturbation theory. Similar computations involving positive and negative centers at opposite ends of the molecule were unsuccessful due to SCF convergence difficulties. The  $2^{3}A'(\pi^{+} \leftarrow \pi)$  excitation is stabilized in the presence of NH<sub>4</sub><sup>+</sup> by only 0.29 eV due to the increased splitting between the primary one-



Fig. 10. The three-dimer configurations used to computationally approximate the intermolecular interactions in the truncated crystal pairing scheme of fig. 9. Although the planar sandwich pairings in fig. 9 show the PNA long axes aligned, the twisted planar structure of dimer 2 was used to approximate the experimental slipped stacking along this axis. electron components contributing to the CI scheme of the free-molecule. Furthermore, the direction and relative magnitude of shift for all excitations of interest were found to be in agreement with results obtained from eqs. (32) and (35) for the free-molecule.

To complete this section it remains to demonstrate that perturbations to the neutral free-molecule electronic structure arising from the crystal environment can also be rendered in terms of the above approximations. Since we choose to simulate the crystal effects computationally in terms of a series of dimer models we are necessarily restricted to PNA systems as the basis function requirements for corresponding DMPNA structures exceed our program limitations. The detailed PNA crystal structure according to Donohue and Trueblood [68] shows, for example, that molecules are arrayed in such a fashion that the five nearest neighbors of each functional group (D<sup>+</sup>-amino/A<sup>-</sup>-nitro) are functional groups of opposite character. This selective charge distribution (group pairing) is, therefore, exactly analogous to the situation encountered for polar fluids. Our approximation to the crystal arrangement is shown in fig. 9.

To properly treat the condensed phase of PNA within a computational scheme one, therefore, would have to consider at least the truncated arrangement of fig. 9. This, of course, is impossible under our present limitations. A reasonable way to simplify the problem is to investigate a reduced structure of only two or three molecules, characterize the interaction and then extrapolate to the full system. The three planes in fig. 9 essentially define three trimer pairing schems which we shall assume independently perturb the electronic structure of the central molecule. Since we have shown above that within the present context the DMPNA/ PNA properties of interest can be characterized by perturbations to the HOMO and LUMO levels the electrostatic interactions inherent to the end-to-end trimer pairing can be ascertained numerically once it is recognized that changes in the HOMO-LUMO separation of the central molecule of the trimer can be approximated by the LUMO (monomer 1)-HOMO (monomer 2) separation of dimer 1 (fig. 10), i.e. the shaded region defines an interaction zone where the LUMO of monomer 1 is lowered due to the net positive charge on the amino group of monomer 2, whereas the HOMO of monomer 2 is raised due to the net negative charge on the nitro group of monomer 1. This behavior directly extrapolates to that expected for the HOMO and LUMO levels of the central molecule of the trimer. Similar considerations of related systems have verified such an approximation [62]. Resolution of the dimer 1 supermolecule results in terms of monomer components is given in fig. 11. Immediately apparent is that, in line with polar solvent perturbations, end-to-end crystal pairing manifests itself in a red-shift of the  $\Phi_{CT}$  (HOMO-





LUMO) excitation relative to the neutral free-molecule. Although supermolecule computations on dimers 2 and 3 of fig. 10 suggest additional decreases in the central molecule HOMO-LUMO spacing, eigenvalue perturbations arising from these pairing schemes appear to be compensated for by concomitant changes in the  $J_{ij}$  and  $K_{ij}$  integrals as  $E(\Phi_{CT})$  is not significantly altered from the free-molecule value. We may, therefore, conclude that the experimental red-shift ( $\approx 1.0 \text{ eV}$ ) resolved for the  $\Phi_{CT}$  excitation of PNA in going from the neutral free-molecule to the crystal environment [3] is largely of electrostatic origin due to end-to-end pairing. It should be noted that although we have made no serious attempt to optimize geometries,  $\Delta \epsilon$ (monomer)  $-\Delta \epsilon$  (dimer, R = 2.0 Å) = 1.13 eV from fig. 11.

# 4. XPS core-level ionization of the DMPNA freemolecule

Projection of the ten lowest-energy singlet and triplet one-electron excitations of the (Z+1)-system onto the appropriate neutral ground state levels in accordance with eq. (23) assuming  $d_{ij} \ge d_0$  reveals that in the presence of the N1s(NO<sub>2</sub>) and O1s core-holes, for example, only HOMO-LUMO excitations contribute significantly to shake-up intensity (typical values of  ${}^{2}P_{1,2}$ range from 20-40% – intensities arising from other contributions are typically <0.1%). This result,

$$\sum_{i \neq \text{HOMO}}^{\text{OCC}} \sum_{j \neq \text{LUMO}}^{\text{UHOCC}} \langle \chi_j^{N-1} | \phi_i^N \rangle \approx 0, \qquad (40)$$

implies

$$\sum_{\substack{i \neq \text{HOMO } j \neq \text{LUMO}}} \sum_{\substack{\{\chi_j^{N-1} | \phi_i^N\} \approx 0 \quad (i \neq j) \\ \approx 1 \quad (i = j)},$$
(41)

which in addition to satisfying the criterion of eqs. (21) and (22) confirms computationally that a description of the ion-states can be limited to a discussion of HOMO and LUMO levels.

The HOMO and LUMO levels of the various DMPNA systems are compared in fig. 12. We consider the N1s and O1s ionization separately, and use the N1s $(NO_2)$ 



Fig. 12. A schematic representation of the HOMO and LUMO levels of the neutral and indicated ionic species of DMPNA as viewed from above the molecular plane (AO coefficients are given opposite the appropriate center). Also given are the energetics (eV) of the HOMO and LUMO shifts relative to the neutral molecule. core-hole-system as an example to detail the numerical results.

### 4.1, NIs ionization

### 4.1.1. NIs(NO2)

As expected from the presence of the positive charge the one-electron eigenvalue spectrum is shifted downward in energy relative to the neutral molecule. Particularly,  $\Delta \epsilon_{LUMO}$  (6.71 eV) >  $\Delta \epsilon_{HOMO}$  (3.81 eV) in line with the localization of these orbitals relative to the core-hole. This selective orbital shift decreases the HOMO/LUMO gap by 2.90 eV in going from the  $N \rightarrow$ N-1 system. Furthermore, fig. 12 shows that the orbital wavefunctions of the ion are considerably modified relative to the unperturbed species. Specifically, a comparison of the neutral and (Z+1) HOMO levels reveal that not only have the NO<sub>2</sub> group AO coefficients substantially increased, but several of the phenyl-group coefficients have changed sign. Similar perturbations to the LUMO level are also evident.

The nature of these modifications to the one-electron wavefunctions in going from the  $N \rightarrow N-1$  system can be understood by recalling that one of our options to the description of the ion-state was to expand  $|\Phi_{IS}^{N-1}\rangle$  in terms of the basis orbitals of the neutral system. In terms of single excitations,

$$|\Phi_{\rm IS}^{N-1}\rangle = \{c_0 a_i + c_1 a_i^{\dagger} a_i a_k^{\dagger}\} |\Phi_0^N\rangle .$$
(42)

Similarly  $|\chi_i^{N-1}\rangle$  may be expanded in terms of  $|\phi_i^N\rangle$ ,

$$|\chi_j^{N-1}\rangle = \sum_i c_{0i} |\phi_i^N\rangle \,. \tag{43}$$

Providing the HOMO and LUMO levels of the neutral system essentially span the ion-state,

$$|\chi_{j}^{N-1}\rangle = 2^{-1/2} (c_{i} |\phi_{\text{HOMO}}^{N}\rangle \pm c_{2} |\phi_{\text{LUMO}}^{N}\rangle).$$
 (44)

In the case of N1s(NO<sub>2</sub>) ion HOMO level, for example, eq. (44) yields each AO coefficient within 10-20% for  $c_1 = 1.0$  and  $c_2 = 0.5$ .

Inserting a similar expansion of  $|\chi_{LUMO}^{N-1}\rangle$  into eq. (23), assuming  $d_{ij} \ge d_0$ , yields,

$${}^{2}P \propto |2^{1/2} c_{ij} \langle \phi^{N}_{\text{HOMO}} | 2^{-1/2} (c_1 \phi^{N}_{\text{LUMO}} \pm c_2 \phi^{N}_{\text{HOMO}}) \rangle|^2 \\ \propto |c_{ij} c_2|^2 .$$
(45)

For  $c_{ij} \approx 1.0$  and  $c_2 \approx 0.5$ ,  $^2P \approx 20-30\%$  within the limits established above. This value is in reasonable

#### Table 2

The excitation energies (eV) of interest and shake-up intensities for the indicated DMPNA gas phase species.  ${}^{1}E_{CT}$  and  ${}^{3}E_{CT}$  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 double excited configuration

		N1s(NO <sub>2</sub> )	N1s[N(CH <sub>3</sub> ) <sub>2</sub> ]	O1s(NO <sub>2</sub> )	Neutral
1 <sub>Ест</sub>	(A)	2.91	5.34	3.31	4.30
-01	(B)	2.78	5.19	3.20	4.14
<sup>3</sup> ECT	(A)	-0.45	3.73	0.82	3.43
-01	(B)	-0.71	3.00	0.23	2.83
J#	(A)	4.71	4.73	4.32	3.73
2Kn'	(A)	3.36	1.61	2.49	0.87
Eave	(A)	0.39	4.13	1.44	3.65
avg	(B)	0.16	3.55	0.97	3.16
${}^{2}E_{1}^{+}$	(A)	1.59	5.33	2.64	
	(B)	1.36	4.75	2.17	
	(C)	1.60	4.78	2.33	$(x_1, y_2) \in \{x_1, \dots, x_n\}$
${}^{2}E_{2}^{+}$	(A)	0.39	4.13	1.44	
	(B)	0.16	3.55	0.97	
는 한 것 같은 한 것 같은 것 같은 것 같은 것 같이. 이 가지 않는 것 같은 것 같은 것 같은 것 같이 있는 것 같이 있는 것 같이 있는 것	(C)	0.85	3.59	1.14	
<sup>2</sup> P <sub>1</sub>	(A)	38.5	<0.1	22.6	
	(B)	37.4	<0.1	21.9	
	<b>(C)</b>	39.7	<0.1	24.1	
<sup>2</sup> P <sub>2</sub>	(C)	<b>4</b> 9	<0.1	4.6	

agreement with the intensity explicitly obtained from the (Z+1)-system CNDO/S wavefunction.

Up to this point we have implied that the (Z+1)system excitation energies are shifted relative to the neutral molecule according to simple electrostatic perturbations which are manifested totally in terms of  $\Delta \epsilon$ ; differences. Using the one-electron configurations we can now investigate the variation in electron-hole interactions in going from the  $N \rightarrow N - 1$  system in greater detail. It is clear from the arguments above that the ion-state orbitals (HOMO and LUMO) are significantly delocalized relative to the corresponding levels in the neutral system which, according to table 2 leads to large increases in the HOMO/LUMO Coulomb and exchange integrals. Although  $J_{ij'}^{Z+1} > J_{ij}^{N}$ , enhances  $\Delta^3 E_{\rm CT}$  relative to what is expected based on  $\Delta \epsilon$  (HOMO-LUMO) differences while the corresponding (Z+1)system singlet shift is inhibited due to  $K_{ii'}^{Z+1} \gg K_{ii'}^N$ , these effects become largely compensating when the relevant excitations are related through average configuration energies,

$$E_{\text{avg}}^N - E_{\text{avg}}^{Z+1} \approx \Delta \epsilon_{ij'}^N - \Delta \epsilon_{ij'}^{Z+1} .$$
(46)

Therefore, in the case of N1s(NO<sub>2</sub>) ionization where modification of the neutral molecule orbitals appears essential in achieving large shake-up intensities such changes do not significantly contribute to  ${}^{2}E_{1}^{+}$  and  ${}^{2}E_{2}^{+}$ .

According to table 2 the N1s(NO<sub>2</sub>) shake-up satellites are calculated to occur within  $\approx 1.6$  eV of the parent peak. Assuming a peak half-width of the signal as shown in fig. 13 where the component intensity distribution was obtained according to the normalization requirement,

$$P_k + \sum_i 2P_i = 1 . (47)$$

The details of assigning a N1s (NO<sub>2</sub>) relative binding energy in agreement with experiment are discussed in the following section.

## 4.1.2. N1s[N(CH<sub>3</sub>)<sub>2</sub>]

Table 2 and figs. 12 and 13 show that the consequences of N1s  $[N(CH_3)_2]$  core-hole creation are dramatically different from the N1s  $(NO_2)$  case. For example, the HOMO-LUMO gap has increased relative to the free-molecule and the one-electron orbitals are only moderately perturbed – small modifications near



Fig. 13. A comparison of the vapor [22] and condensed phase [15,16] O1s and N1s(NO<sub>2</sub>) 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 N1s(NO<sub>2</sub>) spectra is relative to the single N1s(NH<sub>2</sub>) lines (BE = 0).

the N(CH<sub>3</sub>)<sub>2</sub> group. The theoretical  $E_{avg} = 3.55 \text{ eV}$ and corresponding shake-up intensities of <0.1% reflect the absence of intense low-lying shake-up excitations in the experimental gas phase Nls(NH<sub>2</sub>) spectrum of PNA. From a comparison of the Nls[N(CH<sub>3</sub>)<sub>2</sub>] and Nls(NO<sub>2</sub>) spectra we conclude that the qualitative discussion given in the theoretical section is borne out by our numerical results.

It is clear that the absolute binding energies of the nitrogen peaks cannot be extracted from an all-valenceelectron treatment. However, relative core-level binding energies have been successfully correlated with intramolecular charge distributions of the neutral system according to the well known charge-potential model [48,69]

$$E_{\rm B}^{i} = eV_{i}^{0} = KQ_{i}^{0} + \Sigma_{i}^{0} + i, \qquad (48)$$

where  $Q^0$  is the net atomic charge, K and l are adjustable parameters specific for a particular computational scheme and  $\Sigma_i^0$  is the molecular potential defined as,

$$\Sigma_{i}^{0} = \sum_{i \neq j} Q_{j}^{0} / R_{ij} , \qquad (49)$$

where  $R_{ij}$  is the interatomic separation. Table 3 summarizes the results for selected values of K and I, with and without consideration of the molecular potential.

Of the results given in table 3 the simple relationship of Isaacson [70] ( $\Sigma_i^0 = 0, K \approx 8.0, l = 0$ ) fortuitously delivers the best agreement with the experimental 5.70 eV splitting between N1s(NO<sub>2</sub>) and N1s(NH<sub>2</sub>). Neglect of the molecular potential ( $\Sigma_i^0 = 0, K = 21.4, l = 0$ ) yields binding energy differences approximately three times greater than experiment, while Pauling charges [48] ( $\Sigma_i^0 = 0, K = 5.9, l = 0$ ) and the full charge-potential model ( $\Sigma_i^0 \neq 0, K = 21.4, l = -1.74$ ) significantly underestimate the splitting.

It is well known, however, that additional factors such as differential relaxation energy can contribute to binding energy differences [71]. Hedin and

Table 3

The quantities described in the text used to obtain the various  $N1s(NO_2)-N1s[N(CH_3)_2]$  core-level binding energy differences

	N1s(NO <sub>2</sub> )	N1s[N(CH <sub>3</sub> ) <sub>2</sub> ]	∆Eÿ
Q;	0.512	-0.227	
$Q_i^+$	0.583	0.078	
$\Sigma_i^0$	-7.14	6.03	
$\Sigma_i^+$	0.006	9.927	
$E_{\rm B}^{i} \begin{cases} \Sigma^{\rm O} = 0\\ K = 21.4\\ l = 0 \end{cases}$	10.96	-4.86	15.82
$E_{\rm B}^{i} \begin{cases} \Sigma^{\rm O} \neq 0 \\ K = 21.4 \\ I = -1.74 \end{cases}$	2.08	-0.57	2.65
$E_{\rm B}^{i} \begin{cases} \Sigma^0 = 0\\ K = 8.0 \end{cases}$	4.10	1.82	5.92
-(l = 0)			1 - 2 - 2
$E_{\rm B}^{\rm I} \begin{cases} 2^{-} = 0 \\ K = 5.9 \\ I = 0 \end{cases}$	3.02	1.34	4.36
$E_{\rm rel}^{\rm i}$	4.33	5.20	0.87

Johansson [72] have shown that the relaxation energy can be approximated according to,

$$E_{\rm rel}^i \approx -(e/2) \langle \Psi | V_i^* - V_i | \Psi \rangle , \qquad (50)$$

where  $V_i^* - V_i$  is a relaxation potential in going from the  $N \rightarrow N - 1$  system. Substituting

$$\langle \Psi | V_i^* | \Psi \rangle = \langle \Psi | V_i(Z+1) | \Psi \rangle = V_i^+$$
(51)

and

$$\langle \Psi | V_i | \Psi \rangle = \langle \Psi | V_i(Z) | \Psi \rangle = V_i^0, \qquad (52)$$

we obtain a greater relaxation energy for the N1s [N(CH<sub>3</sub>)<sub>2</sub>] ionization than for the N1s(NO<sub>2</sub>) case in agreement with expectations based on relative electron densities of the groups in question. Although the difference in relaxation energies ( $\Delta E_{rel}^{ij} = 0.87 \text{ eV}$ ) increases the binding energy differences calculated from the full charge-potential model ( $\Sigma_i^0 \neq 0, K =$ 21.4, l = -1.74) the discrepancy between theory and experiment is still rather large. This, however, can be rationalized since K = 21.4 is a value optimized by Siegbahn and co-workers [48] for a different computational scheme. Upon increasing K to 24.0 the relationship,

$$\Delta E_{\rm B}^{ij} = K \Delta Q_{ij}^{0} + \Delta \Sigma_{ij}^{0} + \Delta E_{\rm rel}^{ij}$$
  
=  $\frac{1}{2} [K(3\Delta Q_{ij}^{0} - \Delta Q_{ij}^{+}) + 3\Delta \Sigma_{ij}^{0} - \Delta \Sigma_{ij}^{+}], \qquad (53)$ 

yields a binding energy difference in accord with experiment. Although K = 24.0 is not dramatically different from the value given by Siegbahn et al. [48], further application to the problem of binding energies is necessary to achieve an optimum parameter for the CNDO/S scheme.

### 4.2. Ols ionization

Upon simulating an O1s(NO<sub>2</sub>) core-hole we obtain essentially the same effects identified for N1s(NO<sub>2</sub>) ionization, although the magnitudes are generally smaller. Fig. 12 illustrates that the HOMO-LUMO gap is decreased in going from the  $N \rightarrow N-1$  system analogous to the N1s(NO<sub>2</sub>) case; however,  $\Delta \epsilon_{ij'} \approx$ 1.0 eV less than calculated in the presence of the N1s core-hole. This is directly attributable to the location of the oxygen centers on the perimeter of the molecule where the stabilization interaction is smaller by a factor of  $R^{-1}$ . Also, an inspection of the wavefunctions reveal that orbital modifications are less severe for O1s ionization which implies  ${}^{2}P(O1s) < {}^{2}P(N1s)$ . The results of table 2 reflect this simple orbital interpretation.

# 5. XPS-core level ionization of DMPNA in the condensed phase

In order to understand the changes in the coreionization spectra in going from the vapor to the condensed phase we refer to the PNA dimer 1 configuration of fig. 10 and again elaborate on the NIs(NO<sub>2</sub>) corehole species. Since a core-ionization process is a strongly localized event perturbation of the amino group (HOMO level of monomer 2) due to  $N1s(NO_2)$  or  $O1s(NO_2)$ ionization in monomer 1, for example, cannot simply be transferred to the donor group of monomer 1 as was done for the neutral system. It is, therefore, meaningful to address the condensed phase ionization process in terms of specific interactions between the monomer 1 ionic wavefunctions and those of the neutral monomer 2 component [73]. Due to the magnitude of the perturbation we expect a significant intermixing of orbitals between the monomer components. A similar situation was encountered in the case of core-ionization of the single molecule. Fig. 14 shows the one-electron dimer orbitals of interest for N1s(NO<sub>2</sub>) ionization where the planes of the two aromatic moieties are slightly displaced. A comparison with the orbitals in fig. 11 permits identification of the level at -13.31 eV as being essentially the HOMO of the free N1s(NO<sub>2</sub>)-ion and the level at -4.77 eV as the LUMO of the neutral monomer. The remaining two orbitals can be characterized as mixtures of the HOMO of the neutral and the LUMO of the ion. This orbital mixing reflects an extramolecular screening of the core-hole by the surrounding molecules. In terms of electron rearrangements we find that upon creation of a N1s(NO<sub>2</sub>) core-hole  $\approx 0.5e$  of valence charge is drawn from the "neutral" monomer to the site of ionization. A comparison of figs. 12 and 14 shows that extramolecular screening of the N1s(NO2) core-hole dramatically reduces the HOMO-LUMO separation relative to the corresponding ionic monomer (2.84 eV versus 4.26 eV) which serves to shift the average configuration energy to -0.25 eV (fig. 15). In addition, it is easily rationalized that including a greater number of



Fig. 14. A schematic representation of the two highest occupied and two lowest unoccupied  $N1s(NO_2)$  equivalent core dimer orbitals as viewed from above the molecular plane. The relative magnitudes of the orbital lobes are drawn proportional to the atomic orbital coefficients.

molecules in the simulation of the solid state could further reduce  $E_{avg}$ . Therefore, assuming the exchange interaction postulated for the free-molecule, and restricting the computation to singly-excited configurations, we obtain  ${}^{2}E_{1}^{+} = -0.25$  eV and  ${}^{2}E_{2}^{+} = 0.95$  eV. It should be noted, however, that because of the increased delocalization of the orbitals due to intermolecular screening the free-ion multiplet splitting may not strictly apply to the extended structure  $(K_{ik} \ge 0 \text{ would})$ serve to decrease  $\Delta^2 E_{1,2}^+$ ). In the absence of a more suitable approximation we retain the multiplet splitting used for the free-molecule and address the coupling between the ionic ground and excited states due to the double excited configuration. It is found that the smaller energy difference between the ground and excited states relative to the vapor phase model leads to a more pronounced interaction thereby enhancing the splitting in agreement with experiment (fig. 13). Although our approximations yield the trends evident in the experimental data, a more detailed SCF-CI computation where additional single and double excited configura-



Fig. 15. A schematic representation of the gas to condensed phase orbital interactions (eV). Excitation energies between the indicated levels are (top and bottom, respectively)  ${}^{1}E_{i\rightarrow j'}$  and  ${}^{3}E_{i\rightarrow j'}$  for the neutral DMPNA monomer, and  ${}^{2}E_{1}^{+}$  and  ${}^{2}E_{2}^{+}$  for the ionic systems.

tions are included appear necessary to achieve quantitative agreement.

Due to the fact that SCF convergence difficulties prohibited explicit computation on O1s dimer structures for reasonable values of R it is instructive from the standpoint of discussing the differences between the solid state N1s(NO<sub>2</sub>) and O1s core-hole spectra to describe the essential feature of the coupling mechanism between the ion and the surrounding molecules in terms of perturbatoin theory already implied by fig. 15. Rearranging the expressions of Gottfried [74] and Salem [75] the second-order correction to  $\epsilon_i^N$ , for example, due to mixing between  $\phi_i^N$  and  $\chi_{i'}^{Z+1}$  is,

$$\Delta \epsilon_{i}^{N} = (\epsilon_{j'}^{Z+1} - \epsilon_{i}^{N})^{-1} |\langle \chi_{j'}^{Z+1} | H' | \phi_{i}^{N} \rangle - \langle \chi_{j'}^{Z+1} | \phi_{i}^{N} \rangle \epsilon_{i}^{N} |^{2} ,$$
(54)

where  $\langle \chi_{j'}^{\ell+1} | \phi_i^N \rangle = S_{ij'}$  is the overlap matrix and  $\langle \chi_{j'}^{\ell+1} | H' | \phi_i^N \rangle = H'_{ij'}$  is the interaction matrix element between the levels in the presence of a core-hole. The orbital shifts indicated in fig. 15 as a function of R are

approximations to the electrostatic first-order correction  $\langle \phi_i^N | H' | \phi_i^N \rangle$ .  $\Delta \epsilon_{ii}^{Z+1}$  is given by interchanging the orbitals and eigenvalues. Since the oxygen atoms are on the periphery of the ionized molecule,  $\langle \phi_i^{\prime \prime} | H' | \phi_i^{\prime \prime} \rangle$ is larger for 1s than for N1s(NO<sub>2</sub>) ionization which leads to the relative situation depicted in fig. 15, i.e. extrapolating the effects explicitly calculated for  $NIs(NO_2)$  ionization to the O1s core-hole state suggests that the shake-up structure accompanying O1s ionization should be similar in the vapor and condensed phases [73]. Our results, therefore, suggest that the differences observed in the heteroatomic core-hole spectra of DMPNA/PNA in going from the vapor to the condensed phase can be attributed primarily to solid state intermolecular electrostatic interactions and atomic overlap factors. In this regard the essential feature of the condensed phase core-hole interaction is the molecular analog of the dynamical screening model developed to elucidate the core-hole spectra of adsorbates [28,76,77].

### 6. Summary and conclusions

This study has demonstrated that the equivalentcore approximation, within the framework of the CNDO/S-CI method, is sufficient to quantitatively describe the complex interactions leading to the intense N1s and O1s core-hole shake-up structure observed in the vapor phase of the  $D^+$ -Ar-Ar<sup>-</sup> molecules, N,Ndimethyl-p-nitroanihile and p-nitroanihine. Furthermore, by modeling the crystal structure in terms of a supermolecule dimer configuration we found that intermolecular interactions account for the dramatic change in the acceptor N1s core-hole spectrum in going from the vapor to the condensed phase. Similar interactions were found to leave the O1s core-hole shake-up structure approximately unchanged relative to the vapor phase results in accord with experiment.

Particularly, we found that the average configuration energy derived from the singlet and triplet-coupled  $\pi^* \leftarrow \pi$  intramolecular charge-transfer excitation reflects the basic energetic behavior of electronic excitation in the presence of an O1s and N1s core-hole for both vapor and solid phase models, and that the localized nature of the molecular orbitals primarily perturbed by creation of a core-hole allowed us to approximately account for the multiplet splitting between the two possible final doublet states characterizing the shake-up processes.

In addition, the explicitly calculated core-hole induced mixing between the HOMO and LUMO  $\pi$  orbitals were found to yield shake-up intensities approximating the experimental gas phase results. However, it was found that coupling between the primary core-hole and the two doublet valence excitations was essential to the interpretation of the changes in the N1s(NO<sub>2</sub>) spectrum in going from the vapor to the condensed phase. Intermolecular electrostatic and overlap effects were shown to be the dominant factors in determining the spectral differences between N1s(NO2) and O1s core-ionization in going from the vapor to the condensed phase.

Finally, it was pointed out that our model of coreionization in the condensed phase was the molecular analog to the substrate induced screening of core-holes in adsorbates recently addressed in the literature.

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### Note added in proof

S. Svensson has communicated a set of gas and solid phase spectra of PNA. These spectra clearly show that there is a satellite neak at the high binding energy side of the NIs(NO2) emission in the gas phase with excitation energy of  $\approx$  1.25 eV. This is in full agreement with our theoretical results and supports our general conclusions. It should be mentioned that the resolved intensity ratio of 1:1.37 (line width ratio of 1:1.87) compares favorably with our calculated ratio of 1:1.39.

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