## CONFIGURATION INTERACTION STUDY OF SHAKE-UP STRUCTURE ACCOMPANYING CORE-IONIZATION OF SUBSTITUTED AROMATIC MOLECULES IN THE VAPOR AND CONDENSED PHASES: NITROSOBENZENE, DIAZOBENZENE DIOXIDE AND THE NO DIMER

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Manifestations of the condensed phase dimer formation on the N Is and O Is core-hole shake-up structure of nitrosobenzene are examined theoretically within the CNDO/S CI equivalent-core approximation. Computations on the nitrosobendimer (diazobenzene dioxide) were performed to simulate the solid state environment. Results obtained using singly excited and singly and doubly excited ("singlet"-coupled) configurations are contrasted to emphasize the importance of correlation contributions. Although *intermolecular* interactions are found to strongly determine the nature of the solid state spectra, the final state energy and intensity distributions are similar for the vapor (monomer) and condensed phase (dimer) systems as observed experimentally. This "accidental" correspondence is discussed in terms of component contributions to the spectral functions. Computations on the N Is and O Is hole states of the nitric oxide (NO) dimer yield results in close agreement with existing condensed phase spectra of NO. Various similarities between the core-hole induced "intermolecular" interactions in the nitrosobenzene dimer and nitric oxide dimer systems are noted and discussed. Finally, comparison of the UPS spectrum of condensed phase nitric oxide with appropriate valence level calculations on the dimer also indicates strong hole-induced "intermolecular" effects consistent with the analysis of the core-level region.

#### 1. Introduction

Recently it has been recognized that core-ionization spectra of molecules in the gas phase may differ considerably from those obtained on the condensed molecular solid [1-4]. Not only does the binding energy of the core-hole state change upon condensation, but the complete spectral function may be altered. *p*-nitroaniline (PNA) is the most prominent example of such a system. In the case of condensed PNA three distinct peaks are observed in the N 1s ionization spectrum; or

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one more than expected in a system with only two types of nitrogen. A single peak was attributed to the amino group, whereas two components with equally high intensity were found for ionization of the  $-NO_2$  group. There is general agreement with the original assignment of the PNA spectrum given by Pignataro and Distefano [5] that the latter feature arises from a shake-up excitation involving charge transfer from the amino (donor) to the nitro (acceptor) group. The intensity and energy of this shake-up excitation changes considerably, however, if the spectrum is taken on the vapor phase species as shown by Banna [1]. Bigelow and Freund [2,3] proposed an explanation of this effect in terms of intermolecular screening induced by strong coupling of the localized ion state to the surrounding neutral molecules. It turned out that calculations on dimer systems resulted in spectral changes relative to the free molecule which were very similar to those observed experimentally when going from the vapor to the solid phase, provided that correlation contributions were included in the analysis [6]. It was possible to show that the active coupling mechanism was not hydrogen-bonding as had been suggested [6].

So far PNA and 2-amino-6-nitronaphthalene [6] are the only examples where both vapor and condensed phase spectra, as well as a series of appropriate calculations, have been reported. To further elucidate the electronic properties leading to vapor-to-condensed phase spectral changes it is worth carrying through an equivalent study on an additional system.

Very recently Slaughter et al. [7] reported the gas phase core-ionization spectra of nitrosobenzene which provides, together with the corresponding solid state spectra of Distefano et al. [8]. another set of spectra on which to test whether solid state dimer interactions reasonably explain the observed changes in the spectral function. Nitrosobenzene is particularly well suited for such a study because it is known that dimers are actually formed upon condensation [9,10]. No monomeric species were detected in a X-ray analysis of the crystal [11]. The dimer is formed by coupling two nitroso groups via a strong N-N bond with 1.32 A bondlength [11]. The crystal exclusively contains dimer molecules with a cis-configuration. This dimer formation is accompanied by a rather strong distortion of the local nitrosobenzene geometry compared to the planar structure of the monomer in the gas phase [12]. The trans-configuration, where the NO-benzene moiety should have a structure similar to the gas phase, is not found in the crystal, although it is not certain whether this configuration is formed in a frozen vapor [11]. However, there is no doubt from an experimental point of view that specific and strong dimer interactions exist in the crystalline solid.

It is therefore somewhat surprising that the core

photoelectron spectra of gaseous and solid nitrosobenzene are rather similar. The purpose of this work is to address this apparent ambiguity. In addition, unlike the case of PNA, where "pairing" occurs between adjacent donor/acceptor moieties (not dimerization in a chemical sense), nitrosobenzene exhibits "strong" dimer interaction between atoms on adjacent acceptor groups. The question is: does the N-N bond formed on condensation influence the core-hole spectra; and if so, why are gas and solid phase spectra so similar? In this connection it is useful, as we shall see in the course of this paper, to compare the spectra of nitrosobenzene dimers ( $d_{NN} = 1.32$ Å [11]) with those of solid NO [13,14], where dimers are formed in the solid with a N-N bond length of  $\approx 2.2$  Å [15,16]. Recently, Tonner et al. [13] reported strong changes in the spectral function upon condensation of NO which were interpreted as being due to intermolecular screening within the NO dimer moiety.

We report in this paper the results of calculations on monomeric and dimerized nitrosobenzene (cis-and trans-configuration), as well as a brief excursion on the relationship to NO dimers, to show the influence of intermolecular bond strengths on the spectral function. Our computations indicate that the similarities between gas and solid phase spectra are "accidental". The nature of the transitions involved in the satellite excitation are significantly different. While in nitrosobenzene the charge transfer between substituent and phenyl group is the important screening process, the intermolecular charge transfer between NO moieties is the dominating mechanism influencing the satellite intensity within the nitrosobenzene dimer. In comparison to the nitric oxide dimer the nature of this intermolecular screening process is discussed. It is shown that electron correlation is important in correctly describing satellite intensities.

## 2. Computational

Calculations were performed within the semiempirical all-valence-electron closed shell CNDO/ S formalism [17,18] including up to doubly excited

configurations [19] using the Pariser-Part approximation [20] to the two-center Coulomb repulsion integrals. Core-ionized species were treated within the equivalent-core approximation [21,22] where the atom to be ionized (atomic number Z) was replaced by the next highest atom in the periodic table (Z' = Z + 1). Convergence was achieved for all N 1s and O 1s monomer and dimer geometric configurations considered. Excited state computations were then performed on the "equivalent-core" closed shell species assuming only singlet coupling between all valence electrons. In all core-ion state calculations which include doubly excited state configurations the 300 lowest energy excitations were selected from 5000 created configurations of proper symmetry. Relative intensities,  $I_{\rm Red}^{\rm i}$ , were obtained within the sudden approximation by projection of the correlated ionstate wavefunction  $(\Psi_{i,\text{Relaxed}}^{\text{lon}})$  onto that of the "frozen" ion state ( $\Psi_{i, \text{Frozen}}^{\text{Ion}}$ ) given in terms of the one-electron orbitals of the neutral system.

# $I_{\text{Rel}}^{\text{i}} \propto \left| \langle \Psi_{i, \text{Relaxed}}^{\text{lon}} \middle| \Psi_{i, \text{Frozen}}^{\text{lon}} \rangle \right|^2$

Projections of the relaxed ion-state wavefunction onto the correlated *and* uncorrelated initial state were performed to examine the importance of correlation contributions [6,23].

The calculations on the valence-ionization spectra were performed using an open shell version of the CNDO/S program [24]. We calculated the lowest energy doublet state of the radical cation self-consistently and then treated the higher excited doublet states by configuration interaction in the basis of determinants created from the one-electron excitations of the ground doublet state. The intensities for the ionization spectrum were calculated from the projection of ground and excited doublet states onto the determinant of the neutral species [25]. For the valence spectra only singly excited states are included.

Molecular coordinates used in the computations were calculated from bondlengths and bond angles given by Pople and Beveridge [26].

Using our semi-empirical wavefunctions we calculated electron density diagrams and electron density difference diagrams [23]. We also calculated bond indices according to a prescription

given by Cohen [27] as discussed in detail elsewhere [28].

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## 3. Results and discussion

### 3.1. Nitrosobenzene monomer (NB)

The computational results for N 1s and O 1s ionization of the nitrosobenzene monomer (NB) are compared in fig. 1 to the experimental gas phase spectra given by Slaughter et al. [7]. Since neutral molecule correlation contributions had little effect on the final state spectra, only the results obtained by projection of the ion states onto the uncorrelated neutral ground state are shown. The computations clearly reflect experiment, particularly with respect to the differences between N 1s and O 1s ionization. For example, a satellite is obtained at 2.6 eV for N 1s ionization and 3.6 eV for O 1s ionization. These energies are in close agreement with the experimental values of 2.43 eV and 3.75 eV, respectively [7]. The experimental O is shake-up features appear asymmetric and broader than the main line, whereas the shake-up band associated with N 1s ionization is considerably sharper. Such relative behavior is reproduced in the computations. As indicated in fig. 1 the asymmetry in the O 1s shake-up spectrum arises from a second relatively intense excitation not present in the N 1s results. In addition, the broad shake-up feature observed in the O 1s spectrum between 10.0 and 15.0 eV is reflected in the computational results. Although a similar intensity pattern is predicted for N 1s ionization, the experimental spectrum was not extended to sufficient energies to allow a similar correlation.

Localization of the orbitals which contribute most strongly to the shake-up interpretation is given in fig. 2. Within the present set of one-electron orbitals the highly excited configuration (19  $\rightarrow$  21) separately accounts for only a small portion (8%) of the shake-up intensity as indicated in tables 1–4. The shake-up transitions thus "gain" the appropriate additional intensity through constructive interference between the highly excited configuration, the ionic ground state and the doubly excited configurations in the final state inten-



Fig. 1. Comparison of the experimental N 1s and O 1s core-hole spectra of gaseous nitrosobenzene with the results of CNDO/S CI calculations on the planar nitrosobenzene monomer (NB).



Fig. 2. Orbital localizations of the indicated nitrosobenzene monomer species as viewed from above the ring plane. The radii of the circles are proportional to the magnitude of the LCAO coefficients.

sity summation (see tables 1 and 2). The complexity of final state interaction is emphasized by the fact that the higher-lying transitions of tables 1-4cannot be represented in terms of a dominant component.

Distefano et al. [8] reported the results of

#### Table 1

The energies and wavefunctions of the ion states of the nitrosobenzene monomer labelled as indicated in fig. 1. The energies are relative to the uncorrelated core-ionized ground state. The wavefunctions are characterized by their CI coefficients and the corresponding determinants given as a set of four numbers in brackets representing orbitals of the equivalent-core ground state. Occupied and unoccupied orbitals are separated by a double siash

State	Energy	Wavefunction	
	(eV)		. <sup>1</sup> .
1	-1.1776	-0.90 904 (0.010.0)	·
		-0.17 264 (0.19)[21.0)	
		÷0.29 250 (19,19)21,21)	
		+0.10 779 (16,19]21,21)	1.00
2	1.4807	0.29 483 (0,0  0,0)	· · · ·
		-0.79 810 (0,19)21,0)	
		-0.12 720 (0,19)[22,0)	
		+0.11 275 (19,20)21,23)	
	1995 (1997) 1997 - 1997 (1997)	÷0.4 199 (19,19)21,21)	
3	3.8048	-0.12 139 (0.0 0.0)	
		-0.37 387 (0.19  22.0)	
		+0.23 924 (0.20123.0)	
		+0.41 249 (0.16)21.0)	
		-0.2 356 (19.19)21.21)	
		+0.4777(19.19121.22)+	
4	6.5300	-0.49 497 (0.19  22.0)	
-		$\pm 0.34998(0.20123.0)$	
Sec. 14		-0.3117(0.160210)	
		-0.36 406 (19,19][21,21)+	:

#### Table 2

Overlap integrals between the ionic and neutral molecule SCF determinants for N 1s ionization of the nitrosobenzene monomer

Ion configuration	Overlap with neutral ground state
(0,0][0,0)	0.7861
(0,19)21,9)	-0.23061
(19,19)21,21)	0.06765
(16,19)21,21)	0.004545
(0,19)22,0)	0.064056
(19,20)21,23)	-0.000009
(0,20][23,0)	-0.0265
(19,19][21,22)	-0.01879
(0,16  21,0)	-0.01549

# Table 3

The energies and wavefunctions of the O 1s ion states of the nitrosobenzene monomer (see caption to table 1)

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-0.82 -0.96 007 (0,010,0)	
+0.17 504 (19,19)21,21)	
2 2.7184 0.12 173 (0,0][0,0]	
+0.85 473 (0,19)21,0)	
+0.17 982 (0,20)22,0)	
+0.31 855 (19,19)[21,21)	
-0.17 185 (19,20)[21,22)	
4.7906 0.58 013 (0,20)[22,0)	
+0.3 937 (0,19][23,0)	-1119-11
-0.36 319 (0,15  21,0)	ст. <b>Т</b> .
-0.37 144 (20,20)[21,21)	 -
5.5536 0.30 693 (0,20)22,0)	•
+0.40 829 (0,15)[21,0)	
+0.55 818 (19,20)21,22)	
-0.33 317 (20.20)21,21)+	

#### Table 4

Overlap integrals between the ionic and neutral molecule SCF determinants for O 1s ionization of the nitrosobenzene monomer

Ion configuration	Overlap with neutra	
(0,0][0,0)	0.70 983	
(19,19)21,21)	0.136 309	
(0,19  21,0)	0.311 056	
(0,20)22,0)	-0.012 688	وأعاصر أدراجه أر
(0,19][23,0)	0.0168744	
(20,20][21,21)	0.000024	1000 - 100 -
(19,20)21,22)	0.0000204	
(0,15)21,0)	0.143 802	

CNDO/S CI calculations on the nitrosobenzene monomer where only singly excited configurations were considered. The one-particle energies calculated by Distefano et al. differ from ours due to variations in parameterization. The N 1s and O 1s shake-up energies obtained within the singly excited scheme are higher than the present values by  $\approx$  1.0 and 0.7 eV, respectively. In addition, the N 1s and O 1s shake-up intensities given by Distefano et al. are considerably smaller than those shown in fig. 1. We attribute these differences to the inclusion of doubly excited configurations in the present analysis. Nevertheless, the present interpretation as to the nature of the most intense shake-up



Fig. 3. Electron density difference maps of various ground and excited states of the N 1s ionized nitrosobenzene monomer (see text).

features parallels the assignment given by Distefano et al. [8].

To illustrate the nature of the ion states which lead to the N Is spectral function appropriate electron density difference plots are given in fig. 3. Fig. 3a shows the difference between the core-hole ground state and the ground state of the neutral system. Solid lines represent electron gain in the ion, whereas dashed lines correspond to electron loss. The surface on which the electron densities are indicated lies 0.5 Å above the molecule in order to include changes in z-electron density for which the molecular plane corresponds to a nodal plane. Clearly the plot shows a screened ion ground state where a screening charge of 0.803 e accumulates on the ionized nitrogen. The gross atomic populations, as well as the bond orders calculated according to Cohen's [27,28] proposal are given in fig. 4. Obviously the entire molecule contributes to the screening of the ionized center. Fig. 3b indicates, however, that upon electronic excitation 0.24 e is transferred back from the NO moiety towards the benzene ring. It should be noted that an interpretation of the shake-up process in terms of the orbital localizations given in fig. 2 suggests just the opposite direction of charge transfer, i.e. from the aromatic ring toward the NO moiety. The origin of this counter-intuitive result lies in the fact that the final excited state is not pure, but rather a mixture of five determinants (table 1). The charge distribution is given by the square of the complete wavefunction, including interference terms. In this case the cross terms dominate. Decomposition of the excited state charge transfer into atomic components reveals that the oxygen atom contributes 0.2 e (75% of the total excited state charge transfer), whereas the nitrogen looses only 0.04 e (25% of the charge transfer). The ionized N atom then carries only 5% less screening charge in the excited state than in the ionic ground state. Shake-up excitation yields an unscreened oxygen center, even with respect to the neutral ground state. The manifestation of charge transfer from the oxygen atom on shake-up



Fig. 4. Atomic electron densities (circled) and bond orders ( $\pi$ -bond order in parentheses) for the uncorrelated ground states of the neutral, N 1s ionized and O 1s ionized nitrosobenzene monomers.

excitation is quite similar to the situation found for N 1s (NO<sub>2</sub>) ionization of PNA. It should be noted, however, that in PNA excited state charge transfer from the oxygen is to the center of ionization rather than the ring. In PNA it is interference between the NO<sub>2</sub> (oxygen) and NH<sub>2</sub> charge transfer that induces the intense satellite. This explains why nitrobenzene, where only oxygen transfer is possible, does not exhibit intense satellite structure. The electron density difference plots for the higher-lying shake-up satellites of interest are given in figs. 3c and 3d. These are characterized by a charge transfer from the benzene ring toward the NO moiety. In these states the nitrogen atom carries a screening charge larger than in the ionic ground state. The "extra" screening in these states is delivered by the  $\pi$  electrons in the C-C and the C-N bonds. One can speculate that the molecule dissociates when these states are excited.

Figs. 5a-5d show the corresponding electron density difference plots for O 1s ionization. The core-ionized ground state (fig. 5a) carries a screening charge of 0.708 e on the oxygen center. The nature of the most intense O 1s satellite parallels that found for N 1s ionization. The orbitals of the O 1s core-ionized species again suggest a rather massive charge transfer from the phenyl ring toward the NO moiety (see fig. 2 and table 3). Due to the nature of the cross terms appearing in the charge density evaluation, interference effects like those noted for N 1s ionization inhibit excited state charge transfer. As indicated in fig. 5b, there is essentially no net charge transfer. The electron density difference given in fig. 5b can be viewed as a "charge density oscillation" moving between the extremes of the molecule. The higher excited O 1s satellites also exhibit similarities with the N 1s results. Again, there is negligible charge transfer between the phenyl and NO groups. The second shake-up state is more intense than the corresponding N 1s transition because the projection of orbital #15 onto the LUMO level is much larger. The satellites accompanying O 1s ionization appear at higher energy than the corresponding N 1s features due to a larger HOMO-LUMO gap and the stronger stabilization of orbital #19. This latter selective interaction is caused by the contracted oxygen functions which led to an enhanced

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Fig. 5. Electron density difference maps of various ground and excited states of the O Is ionized nitrosobenzene monomer (see text).

Coulomb stabilization upon ionization for the levels localized on the NO moiety. It is worth noting that the differences in HOMO-LUMO separation for O Is and N Is ionization are less dramatic than found for PNA, for example.

## 3.2. Nitrosobenzene dimer

In order to theoretically address the photoelectron spectra of solid nitrosobenzene, computations must at least account for the cis-dimer pairing as indicated by X-ray diffraction studies [11]. Therefore, spectral functions of the cis-isomer of the unsubstituted dimer were calculated based on a model drawn from the experimental geometry [11]: a planar  $O \leftarrow N-N \rightarrow O$  cis-configuration (<NNO = 120°); 1.32 Å N-N separation; and, phenyl groups rotated 90° relative to the NO-NO plane. Fig. 6 compares the N Is and O Is ionization spectra of the cis-nitrosobenzene dimer obtained with and without neutral ground state correlation. Fig. 6 indicates that correlation in the neutral dimer species contributes significantly to the final state dimer shake-up intensities, as opposed to the monomer case where such contributions were found to be minimal. As indicated in the top panel of fig. 6 low-lying shake-up features accompanying N 1s ionization are completely absent when initial state correlation is neglected. The relative contribution of double excitations to the neutral dimer ground state is indicated in table 5.

In the case of N 1s ionization of the monomer the intense shake-up feature was induced by an interference of phenyl  $\rightarrow$  NO and oxygen  $\rightarrow$ nitrogen  $\pi$ -electron charge transfer. Due to the twisted configuration of the cis-dimer charge transfer between fragments is inhibited in the solid state. A detailed account of NO-NO interaction is thus essential to describe the condensed phase N Is shake-up structure. Analysis of the O 1s monomer spectrum, however, revealed that phenyl  $\rightarrow$ NO charge transfer did not participate as strongly

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Fig. 6. Comparison of the theoretical N 1s and O 1s core-hole spectral functions of the cis-nitrosobenzene dimer obtained with and without neutral ground state correlation.

in the shake-up process as found for N 1s ionization. Specific NO-NO interaction should, therefore, be of less consequence to the O 1s cis-dimer spectral function. This conclusion is reflected in fig. 6 where considerable O 1s intensity is also calculated when ground state correlation is neglected.

The wavefunctions of interest for N 1s and O 1s cis-dimer ionization are given in tables 5 and 7, respectively. The localization of relevant dimer orbitals is given in fig. 7. First, the interaction

## Table 5

Energies and wavefunctions of appropriate N 1s ion states of the cis-nitrosobenzene dimer compared to the correlated neutral ground state; energy relative to the neutral species SCF ground state. The ion state labels correspond to the features given in the top panel of fig. 6 (see caption to table 1)

State	Energy (cV)	Wavefunction
ground state	-1.174	0.92 614 (0,0][0,0)
neutral		-0.32 984 (40,40] 41,41)
ion state 1	-0.61	0.95 661 (0,0)0,0)
No. 11 Concerns		-0.15 745 (0.37[41,0)
		-0.14 405 (37,37)41,41)
ion state 2	1.48	0.20 382 (0,0][0,0)
		÷0.88 537 (0,37][41,0)
		+0.14 663 (0,38 41,0)
		+0.33 144 (37,37[41,41)

#### Table 6

Overlap integrals between ionic determinants of the N ls ionized cis-nitrosobenzene dimer and (i) the neutral dimer SCF determinant, (ii) the corresponding doubly excited determinant created by (40,40][41,41) excitation; the numbering system refers to orbitals of the neutral dimer SCF determinant

Ion configuration	Overlap with SCF determinant of neutral ground state	Overlap with doubly excited configuration (40,40  41,41)
(0.0][0.0)	0.73 394	0.137 171
(0,37)41,0)	-0.24 150	0.306 534
(0,38[[41,0)	-0.040 884	0.523 313
(37,37 41,41)	0.079 465	0.685 009

leading to dimer formation can be understood in terms of fig. 7. For example, the HOMO and LUMO dimer levels are formed by combining the antibonding NO  $\pi$  orbitals to yield a bonding and antibonding combination (orbitals #40 and #41 in fig. 7). Due to steric hindrance these NO levels do not couple to the phenyl ring orbitals, specifically orbital #21 of fig. 2, as found in the monomer. In the one-electron picture the dimer is stabilized by doubly occupying the bonding combination. Also, the determinant formed by doubly occupying the antibonding combination is only 4.92 eV higher in energy. Since the two states have the same symmetry a strong interaction occurs which leads to a ground state stabilization of 1.17 eV. Subsequent to interaction the ground state wavefunction achieves approximately 11% doubly excited character.

## Table 7

Energies and wavefunctions of appropriate O Is ion states of the cis-nitrosobenzene dimer compared to the correlated neutral ground state; energy relative to the neutral dimer SCF ground state. The ion state labels correspond to the features given in the bottom panel of fig. 6 (see caption to table 1)

State	Energy (cV)	Wavefunction
ground state	-1.174	0.92 614 (0.9][0.0)
neutral		-0.32 984 (40,40[]41,41)
ion state 1	-0.57	0.97 919 (0,0[[0,0]
ion state 2	4.45	0.83 986 (0,36j;41.0)
		-0.22 975 (0.40[[42,0)
		÷ 0.17 939 (0.40[[44.0)
n de la composition d La composition de la c		+0.15 149 (0.35[41,0)
· · · · · · · · · · · · · · · · · · ·	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 -	+ 0.31 645 (0.33]]+1,0)
		-0.15 708 (0.37[44.0)
		-0.16 040 (36,36]41,41)
ion state 3	6.94	0.22 073 (0.40[41.0)
		- 0.38 624 (0.39[[45.0]
		-0.31 538 (0.38[43.0)
		+0.31 240 (0.33]41.0)
		-0.40 315 (0.37[42,0)
		÷0_38 436 (0.40įį48.0;

Table S

Overlap integrals between ionic determinants of the O 1s ionized cis-nitrosobenzene dimer and (i) the neutral dimer SCF determinant. (ii) the corresponding doubly excited determinant created by (40,40[[41,41] excitation; the numbering system refers to orbitals of the neutral dimer SCF determinant

Ion configuration	Overlap with SCF determinant of neutral ground state	Overlap with double excited configuration (40,40][41,41)	
(0,000,0)	0.77 763	0.15 506	
(0.36[41.0)	0.201 599	-0.243 189	
(0.40[[42.0)	-0.014 902	-0.002 972	
(0.40/44.0)	-0.0 573 707	- 0.047 459	
(0.35141.0)	-0.063 742	-0.047 459	
(0.33141.0)	-0.16 703	0.1 816 303	
(0.37544.0)	0.006 591	0.0 013 143	
(36.36)(41.41)	0.052 264	0.381 408	
(0,39[[45,0)	0.020 978	0.004 196	

Upon creation of an N 1s core hole the niupgens are no longer equivalent. This leads to a relative localization of the one-electron wavefunctions on specific "fragments" of the dimer. The occupied orbital, for example, is localized on the NO moiety containing the core hole which implies a transfer of charge toward the ionized atom. This is demonstrated more directly by comparing charge distributions in the neutral and the N 1s ionic ground state. Fig. 8 shows gross atomic populations and bond indices for the N<sub>2</sub>O<sub>2</sub> region. A screening charge of 0.94 e is drawn toward the ionized nitrogen atom, 67% of this charge comes from the non-ionized or "neutral" NO moiety with the remainder derived from the phenyl group. Although the occupied and virtual ion levels of interest are localized on different parts of the N<sub>2</sub>O<sub>2</sub> region, their phase relatio, parallels that of the neutral system orbitals. An excited state of the ion, with orbital #41 occupied, is therefore likely to have a small overlap with the uncorrelated neutral ground state. The correlated ground state, however, contains a determinant where the antibonding "N<sub>2</sub>O<sub>2</sub> orbital" is occupied. The overlap between this component and the excited ion state therefore is expected to be larger (see table 6). The result is that the satellite gains intensity through ground state correlation (see fig. 6).

As noted above, corresponding interactions within the O 1s ionized dimer are less pronounced. The accumulation of screening charge on the ionized oxygen is less (0.49 e) than calculated for N 1s ionization (see fig. 8). O 1s ionization, however, leads to a similar localization of one-particle wavefunctions as found in the N 1s ionized system. The main difference between N 1s and O 1s ionization appears to arise from interference terms involving overlap amplitudes between the correlated neutral ground state and components of the ionic ground and excited states. As indicated in tables 6 and 8 overlap of the ionic terms with the primary ground state determinant, (0,0||0,0) are in phase for O 1s ionization, but out of phase for N Is ionization. The reverse condition is found for overlaps involving double excitation of the neutral system.

Fig. 9 compares the ion-state spectral functions calculated for the cis-dimer and a hypothetical trans-dimer configuration with the experimental solid state spectra [8]. Computations on the transisomer are included to provide some indication of the sensitivity of shake-up structure on increasing the interaction between the NO-NO part and the phenyl groups. Although the unsubstituted trans-



Fig. 7. Orbitals of the neutral, N 1s ionized and O 1s ionized uncorrelated ground states of the cis-nitrosobenzene dimer as viewed from above the molecular plane. The circles are proportional to the LCAO coefficients. The ionized atom is marked by an asterisk.

dimer is not found in the crystal, computations were performed on a construction derived from the geometry of an experimentally confirmed trans-dimer species of a suitably substituted nitrosobenzene [11]. Our model of the trans-dimer assumed phenyl group rotations of only 30° from the NO-NO plane. The agreement between theory and experiment shown in fig. 9 is not as good as obtained for nitrosobenzene in the gas phase. Certain "trends" on going from the vapor to the solid are, however, adequately represented by the cis-dimer model. For example, the relative O 1s shake-up intensity is decreased from 62% to 48% upon condensation [7,8] in comparison to the calculated decrease of 52% to 26%. In addition, the computations indicate a 1.3 eV increase in satellite energy on going to the solid compared to the experimental value of 0.25 eV. Although computations indicate a 0.5 eV shift in the N 1s shake-up peak to lower energy with an accompanying loss of intensity on going to the solid which is contrary to experiment, the relative influence of dimer formation on the N 1s and O 1s shake-up energies is correctly given.

Corresponding studies on PNA [2,3,6] and 2amino-6-nitronaphthalene [6] have shown quite good agreement between calculated and experimental differences in heteroatomic core-hole structure on going from the vapor to the condensed phase. It is worthwhile to comment on possible origins of the generally less impressive comparisons obtained in the present analysis. For example, it is possible that when the solid is prepared by condensation of the nitrosobenzene vapors onto a cooled substrate the dimer is incompletely formed, or that a precursor state is achieved with



Fig. 8. Atomic electron densities and bond orders for the neutral. N 1s ionized and O 1s ionized uncorrelated ground states of the cis-nitrosobenzene dimer. Values are only given for the  $N_2O_2$  moiety and the attached carbon atoms. The ionized atom is indicated by an asterisk.

an enlarged N-N separation. A careful X-ray photoelectron spectroscopic study of well characterized nitrosobenzene molecular crystals would provide conclusive information on dimeric contributions to intermolecular screening. Consideration of a single dimer pairing may also be inadequate. A theoretical aspect likely to be of even greater significance is the lack of size consistency in the CI evaluation of the monomer versus the dimer structure. The number of excited configurations included in the monomer and dimer computations were identical, i.e. 300 singly and doubly excited configurations. However, since the number of orbitals are doubled on going to the dimer, certain higher-lying excitations addressed in the monomer computations are neglected in the larger system. The excited dimer states are therefore not as completely described as those in the monomer. Inclusion of a larger number of configurations in the dimer problem may well influence the relative shake-up intensities and energies. The problem of size consistency is further addressed in the following section.

## 3.3. NO-dimer

In order to reduce the magnitude of the sizeconsistency problem and to address the issue of "partial" dimer formation upon condensation of nitrosobenzene, corresponding computations were performed on the nitric oxide dimer, (NO)2. Neglect of the phenyl groups appears to be a suitable approximation in a detailed analysis of the "localized" NO-NO interactions. Although some screening charge was drawn from the aromatic moieties in the O 1s and N 1s ionic ground states of the cis-nitrosobenzene dimer, excitations involving the phenyl group orbitals were found to have a negligible effect on the resulting shake-up structures. The comparison computations noted above on the trans-nitrosobenzene dimer further indicates an absence of significant phenyl group contributions to the satellite structure, i.e. a rotation of the phenyl groups toward greater planarity with the NO-NO projection yields an O 1s shake-up structure without a distinct peak. This result is contrary to experiment as shown in fig. 9. Although the one-electron coupling within the NO dimer is found to be somewhat different from the NO-NO coupling within the nitrosobenzene dimer, sufficient parallels exist to permit us to qualitatively examine spectral consequences of partial bond formation in the latter system by varying the bond distance in the NO dimer.

Fig. 10 shows the calculated N 1s and O 1s hole-state spectra of  $(NO)_2$  for the indicated equilibrium geometry [15,16,29–31]. The influence of doubly excited states is clearly demonstrated. As indicated in fig. 11 a rather weak  $\sigma$  bond is formed by interaction of the in-plane components





Fig. 9. Comparison of the experimental N 1s and O 1s core-hole spectra of solid nitrosobenzene with the results of calculations on the cis- and trans-nitrosobenzene dimers including ground state correlation.

of the two singly occupied  $2\pi^*$  orbitals of NO [13,14]. The orbital corresponding to the  $\sigma$ bond constitutes the HOMO level whereas the o\* virtual level derived from bonding interactions becomes the dimer LUMO level. The two out-ofplane  $2\pi^*$  components form  $\pi$  orbitals and are not occupied. Upon ionization a screened hole state is formed as exemplified for the N 1s core hole in fig. 12a. The total screening charge of 1.08 e accumulated on the ionized atom is derived from the adjacent oxygen atom (24%) and the "neutral" NO moiety (76%). This characterizes the ionic ground state of the NO dimer as an intermolecular screened state, similar to the situation found for the nitrosobenzene dimer. The charge distribution corresponding to the rather intense N Is shake-up feature obtained when neutral ground state correlation is included is shown in fig. 12b. Clearly, charge is transferred back to the "non-ionized" moiety through the  $2\pi^*$  channel (see the ion-state

orbitals of fig. 11). The reverse charge-transfer in the N 1s shake-up state amounts to 56% of the ground state screening charge. This result is in essential agreement with the conclusions of Tonner et al. [13]. Tables 9 and 10 reveal that the large influence of initial-state correlation arises from the large overlaps involving the doubly-excited configuration contributing to the neutral molecule ground state where the  $\sigma$ -character antibonding  $2\pi^*$  orbital is occupied.

At this point the correspondence between the NO and nitrosobenzene dimers becomes obvious: if the geometry of the NO dimer is changed simply by enlarging the intermolecular separation the energy and intensity of the primary N 1s shake-up feature is modified (as indicated in fig. 13). The right-hand panel of fig. 13 graphically shows the variations for the two core-hole lines resulting from N 1s ionization. As the interaction between NO moieties becomes less, the splitting between



Fig. 10. Comparison of the experimental N 1s and O 1s core-hole spectra of solid nitric oxide with the results of calculations on the nitric oxide dimer. Results using correlated and uncorrelated wavefunctions for the neutral species are given.

#### Table 9

Energies and wavefunctions of appropriate N 1s ion-states of the cis-nitric oxide dimer compared to the correlated neutral ground state; energy relative to the neutral dimer SCF ground state. The ion state labels correspond to the features given in fig. 10 (see caption to labe 1)

State	Energy (eV;	Wavefunction
ground state	-1.560	0.92 875 (0.0[0.0)
neutral		-0.33 336 (11.11g12.12)
ion state 1	-1.22	-0.97 318 (0.0 0.0)
	e de la composición d En composición de la c	+0.13 299 (10,10#14,14)
ion state 2	3.22	0.94 133 (0.11)13.0)
		+0.25 362 (11,11)13,13)
ion state 3	12.29	-0.29 182 (0,9913,0)
a de la composition de		+0.20 309 (0.8/12,0)
		-0.12 330 (10,11)13,14)
1. <sup>11</sup>		-0.62 802 (0.10)14.0)
		-0.40 459 (0,6613.0)
		-0.37 164 (0,5113,0)
		-0.20 596 (10,11)13,14)
		+0.18 215 (0,4 113,9)

#### Table 10

Overlap integrals between ionic determinants of the N 1s ionized cis-nitric oxide dimer and (i) the neutral dimer SCF determinant, (ii) the corresponding doubly excited determinant created by (11,11][12,12) excitation; the numbering system refers to orbitals of the neutral dimer SCF determinant

Ion configuration	Overlap with SCF determinant neutral ground of state	Overlap with double excited configuration (11,11][12,12)
(0,0][0,0)	0.710 848	0.220 302
(10,10)14,14)	0.023 687	0.007 341
(0,11113,0)	-0.357 381	0.394 778
(11,11][13,13)	0.179 675	0.707 436
(0,9113,0)	-0.095 326	0.045 901
(0,8112,0)	-0.012 222	-0.003 788
(10,11913,14)	0.065 238	-0.072 064
(0,10114.0)	-0.129 761	-0.040 215
(0,6113,0)	0.019 965	-0.0193 629
(0,5)13,0)	-0.061 931	-0.0720 641
(0,4913,0)	0.0 004 224	0.0 061 308
(10.11)13.14)	0.065 238	-0.070 641



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Fig. 11. Orbital localizations for the uncorrelated neutral and N 1s ionized ground states of the nitric oxide dimer as viewed from above the  $N_2O_2$  plane. Atomic electron densities as well as bond orders for the two states are also given.

features is reduced concomitant with an increase in satellite intensity. At larger separations the satellite corresponds to an *intramolecularly* screened state. The satellite should thus gain intensity as the NO moieties achieve greater "monomer-like" character. When the interaction is rather strong the satellite intensity is reduced since *intermolecular* screening dominates.

Since the NO dimer and nitrosobenzene dimer satellite intensities are experimentally similar, a similar ON-NO bond strength is expected in the two systems. A comparison of heats of dimerization indicates that this is indeed the case: 0.05 eVfor the nitrosobenzene dimer [9], and 0.07 eV for (NO)<sub>2</sub> [15,16]. In the case of the nitrosobenzene dimer, however, the total binding energy is a superposition of the NO-NO interaction, and the destabilizing interaction involving the phenyl rings. If the phenyl groups are assumed to avoid each

other, i.e. as in  $\alpha$ -nitrosotoluene where CH<sub>2</sub> groups "isolate" the NO groups from the phenyl rings, the total binding enthalpy increases dramatically: 0.05 eV versus 0.87 eV [9]. On the basis of this result a rather small nitrosobenzene dimer satellite intensity is expected which is neither observed or calculated (see fig. 9). This apparent ambiguity can be resolved through a comparison of the relevant dimer orbitals. As noted above, fig. 11 clearly shows that the (NO), shake-up occurs within the manifold of  $\sigma$  orbitals formed by weak interaction of the two in-plane  $2\pi$  orbitals. The "weakness" of this coupling determines the satellite intensity. On the other hand, the  $\sigma$  interactions between nitrosobenzene moieties is much stronger due to the shorter N-N bondlength. The main contributions to the nitrosobenzene dimer shake-up, however, are  $\pi$  electrons as outlined above. The coupling between the  $2\pi$  orbitals in the dimer is





Fig. 12. Electron density difference plots of the ground (a) and most intense shake-up (b) state of N 1s ionized  $(NO)_2$ . The maps are plotted in the NO-NO plane.

indeed much weaker than the accompanying  $\sigma$ interaction. The NO–NO  $\pi$  orbital coupling in the nitrosobenzene dimer is, in fact, comparable in magnitude to the  $\sigma$  coupling in (NO)<sub>2</sub>. The interactions leading to the high core-hole satellite intensity observed for the nitrosobenzene dimer thus parallels the analysis of the (NO)<sub>2</sub> shake-up features, in spite of the shorter bondlength achieved in dimer formation. Variation of the magnitude of ON–NO coupling within the nitrosobenzene dimer would produce results similar to those shown in fig. 13 for (NO)<sub>2</sub>.

Further evidence indicating the significance of "intermolecular" electronic coupling between components of the NO dimer is given by the appearance of new features in the valence ionization spectrum on going from the vapor to the condensed phase [13,32] (see fig. 14). Condensation yields a reduced intensity peak  $\approx 2.2 \text{ eV}$ above the first ionization band which is absent in the eas phase. In accord with experiment open shell CNDO/S CI computations on the valence level ion states of (NO), yields a weak intensity, or shake-up feature, at  $\approx 3.2$  eV above the first ionization (see fig. 14). In line with symmetry arguments [33], the computations indicate that the solid state induced low-lying shake-up arises from coupling between the HOMO  $\rightarrow$  LUMO excited







Fig. 14. Comparison of the experimental valence ionization spectrum of solid NO with results of an open shell CNDO/S CI computation on  $(NO)_2$ . The spectrum of gaseous NO is given for comparison.

configuration and the second primary hole state obtained by ionizing the second highest occupied dimer orbital. The HOMO and LUMO orbitals of the valence-ionized dimer are generated from coupling between the in-plane NO  $2\pi^*$  components, and thus correspond to those levels which are of particular importance in the elucidation of core ionization. The primary hole configuration from which the valence level shake-up state of interest receives intensity is likewise derived from ionization of an in-plane orbital. Further analysis of the valence spectrum is in progress [34].

## 4. Summary and conclusions

Theoretical N 1s and O 1s core-ionization spectra of monomeric nitrosobenzene and a model nitrosobenzene dimer structure were calculated within the CNDO/S CI equivalent-core approximation with allowance for up to doubly excited configurations and favorably compared to existing vapor and condensed phase spectra. Unlike the dramatic differences in core-hole structure observed for some donor/acceptor-substituted aromatic systems on going from the vapor to the condensed phase, the satellite structures for N 1s and O 1s ionization of nitrosobenzene are relatively unchanged upon condensation even though specific intermolecular interactions are experimentally indicated for the solid. Our analysis indicated that such a similarity was "accidental" due to different coupling mechanims active in the two cases

Specifically, the theoretical results for the planar monomer ionizations were in excellent agreement with observation. Intense satellite structure for both O Is and N Is ionization, at the approximately correct energies, were obtained. The nature of the satellite features were analyzed in terms of interactions between the aromatic and nitroso groups. Neutral molecule ground state correlation had little effect on the final state spectra. Computations on the dimer structure provided less quantitative agreement with the condensed phase spectra, although subtle energy and intensity variations noted experimentally on going to the condensed phase were qualitatively reproduced. The

dimer geometry used to model the condensed phase environment was derived from the experimental crystal structure where specific NO-NO cis-dimer pairing was indicated, with the phenyl groups rotated  $\approx 90^\circ$  out of the NO-NO plane. The less than ideal agreement between theory and experiment pointed out the importance of a careful X-ray photoelectron spectroscopic study on molecular crystals of the nitrosobenzene dimer (diazobenzene dioxide) to unequivocally demonstrate the influence of well characterized intermolecular interactions on the core-hole structures. Computations, nevertheless, indicated that solid state shakeup arises from intermolecular screening between the coupled NO moieties, and is thus quite different in origin than found for the gas phase species. The importance of neutral ground state correlation in the description of the condensed phase spectra was also demonstrated. Comparison computations on a hypothetical trans-nitrosobenzene dimer. where the phenyl moieties were only rotated 30° from the NO-NO plane, further verified the lack of significant aromatic group contributions to the condensed phase shake-up structure.

To further elucidate the consequences of "localized" NO-NO coupling on the nitrosobenzene condensed phase spectra the N 1s hole-state spectral function of the nitrous oxide dimer was examined. Intense satellite structure was attributed to intermolecular screening factors in accord with prior theoretical arguments. Although relative satellite intensity was shown to be strongly dependent on N-N separation, the final state intensity and energy distribution calculated at the equilibrium geometry was in close agreement with experiment. Parallels between the nature of the coupling in (NO)<sub>2</sub> and in the nitrosobenzene condensed phase and crystal habit were indicated.

Further evidence indicating the significance of "intermolecular" electronic coupling between components of the NO dimer was obtained through a comparison of the existing UPS condensed phase spectrum with semi-empirical open shell computations in the valence level ion states. Orbitals derived from solid state interaction, and which contribute to the experimentally well-resolved valence level shake-up peak, were found to correspond to those levels which were of particular importance in the determination of the core-hole shake-up features.

Finally, the present study emphasized that analysis of solid state core-hole spectra based on computations restricted to an isolated molecule model may lead to misleading interpretations.

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