Abstract: The O1s and N1s vapor-phase photoelectron spectra of N,N-dimethyl-p-nitrosoaniline are reported. The O1s spectrum exhibits well-resolved intense multipeak structure. The N1s(NO) and N1s[N(CH3)2] ionizations sum to yield a considerably less structured spectrum. CNDO/S-CI equivalent-core computations yield O1s and N1s spectral functions in essential agreement with experiment. The heteroatomic spectral functions are discussed in terms of dominant singly and doubly excited electronic contributions. The vapor-phase results are compared and contrasted to existing molecular solid-state spectra to address the nature and manifestations of core-hole-induced intermolecular interactions.

It is well-known that the core-level photoelectron spectra of donor/acceptor substituted aromatic compounds in the condensed molecular solid can exhibit intense heteroatomic shakeup structure.1-16 Although numerous quantum chemical studies have provided compelling evidence that intense shakeup satellites are indeed commonly inherent to such systems, modeling of the solid state spectral features is usually given in terms of electronic configurations of the isolated or vapor-phase species.12-18 Recently, however, it was shown that the details of the core-level spectra of aromatic donor/acceptor compounds could be consid-

Figure 7. Ion yields of m/z 15 from (a) CH3CHOH+ and (b) CH3OCH2+ as a function of ion kinetic energy using NH3 collision gas. The line represents the best fit to the theoretical doppler-broadened appearance curve (linear cross-sectional model).

due to the formation of NH2CH20H (rather than HCOH) is CH30CH2+ as a function of ion kinetic energy using NH3 collision gas. Figure due to the formation of NH2CH20H (rather than HCOH) is CH30CH2+ as a function of ion kinetic energy using NH3 collision gas. Figure
erably modified on going from the vapor to the solid phase.19-22 The first and thus far most prominent example of core-level spectral modification accompanying the gas-solid phase transition is given by p-nitroaniline (PNA).19-21 Both the N1s( NO3) and O1s satellite intensities are significantly enhanced. Specifically, the gas-phase N1s(NO3) spectrum is asymmetric, with approximately 30% of the total intensity appearing as a low-lying satellite on the high-binding-energy side of the main peak (ΔE = 1.25 eV). Upon condensation a well-resolved doublet with approximately equal intensity components is observed (ΔE ~ 1.8 eV).

Several interpretations of the gas-solid-state spectral changes have been offered. One involves strong core-hole-induced intermolecular electronic coupling, which increases the screening contributions already active in the vapor-phase species.23-25 It has also been proposed that formation of hydrogen bonds in the solid may perturb the gas-phase orbital energies in a manner that enhances intramolecular coupling of the core-hole and valence excitations.20 Owens and co-workers20 recently noted, and subsequently rejected, the notion that the condensed-phase multiplet N1s(NO3) core-hole spectra of poly(nitroaromatics) were due to asymmetries in the molecular environment. The first mechanism is core-hole induced and thus a final-state effect, whereas the hydrogen bonding interpretation is essentially manifest in the initial state.

In an effort to further resolve this issue vapor-phase core-level photoelectron spectra were recently reported for 2-amino-6-nitronaphthalene (2,6-ANN),22 1-amino-4-nitronaphthalene (1,4-ANN),22 and nitrosobenzene (NB)21 and compared with solid-state results.22,25 Quantum chemical studies on PNA,22 2,6-ANN,22 and NB25 produced gas-solid-state core-level spectral function shifts paralleling experiment. Dimer models were used to simulate the solid-state environment. Fundamental modifi-
cations to the spectral functions due to core-hole-induced intermolecular screening were indicated.

In this work we report the O1s and N1s vapor-phase core-level photoelectron spectra of N,N-dimethyl-p-nitroaniline for comparison with existing condensed-phase results.12,27 N,N-di-

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moyety is known to form well-defined dimers upon condensation, whereas dimethyl substitution of the amino nitrogen is expected to inhibit hydrogen bonding interactions. The heteroatomic spectral functions of the gas-phase species are discussed in terms of dominant electronic configurations based on the results of CNDO/S-CI equivalent-core computations.

Experimental Section

Photoelectron spectra were measured for the NIs and OIs regions of gaseous N,N-dimethyl-p-nitrosoaniline with Al Kα X-rays (1486.582 eV)\(^{32}\). An electrostatic electron spectrometer with a 10-cm mean radius hemispherical analyzer was utilized. The instrument is located at Vanderbilt University and will be described in a forthcoming publication. A commercial reagent-grade sample was used without further purification. The temperature needed to obtain sufficient vapor pressure was \(\sim 80°\)C; this was achieved by using a resistively heated stainless steel oven. The NIs and OIs regions are shown in the top parts of Figures 1 and 2, respectively. Intense shakeup peaks are present in both regions, as expected for this class of molecules.\(^{25-27}\) To obtain relative intensities and separations, Lorentzians or Gaussians as expected for this class of molecules were fitted to the experimental data points using a least-squares program described elsewhere.\(^{30}\) The deconvolution was subject to large uncertainties due to the severe overlap between the various peaks. This is particularly pronounced in the Nls region, since it was not possible to resolve the Nls (NO) peak from the Nls(N(CH\(_3\))\(_2\)) peak. In addition, these peaks overlap the shakeup structure on the high-binding-energy side.

Theory

Spectral functions were calculated within the semiempirical all-valence-electron closed-shell CNDO/S formalism\(^{1,2}\) including up to doubly excited configurations\(^{2}\) using the Pariser–Parr approximation\(^{24}\) to the two-center repulsion integrals. Core-ionized species were treated within the equivalent-core approximation\(^{3,5,8}\) 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 core-hole species considered. Excited-state computations were thus performed on the “equivalent-core” closed-shell species by assuming only pure singlet coupling between all valence electrons. The neglect of core-valence exchange terms and interactions involving “triplet-coupled” configurations is not expected to cause serious deficiencies in spectral interpretation for delocalized systems exhibiting intense shakeup.\(^{9,22,25}\)

In all core-ion-state calculations that include doubly excited configurations the 300 lowest energy excitations were selected from 5000 created configurations of proper symmetry. Relative intensities, \(I_{rel}\), were obtained within the sudden approximation\(^{32}\) by projection of the correlated ion-state wavefunctions \(\langle \Psi_{\text{core}} \rangle\) onto that of the “frozen” ion state \(\langle \Psi_{\text{frozen}} \rangle\) given in terms of the one-electron orbitals of the neutral system

\[
P_{rel} \propto \left| \langle \Psi_{\text{core}} \rangle | \Psi_{\text{frozen}} \rangle \right|^2
\]

Projections of the relaxed ion-state wavefunctions onto the correlated and uncorrelated initial state were performed to examine

\[(34)\text{Pariser, R.; Parr, R. G. Chem. Phys. 1953, 21, 37–75.}
\[(35)\text{Jolly, W. L.; Hendrickson, D. J. J. Am. Chem. Soc. 1979, 92, 1863–1871.}
\[(36)\text{Davies, W. M., Shirley, D. A. Chem. Phys. Lett. 1972, 15, 185.}

\[(40)\text{Herz, U. Phys. Scr. 1979, 24, 9, 133–147.}
Table I. Energies and Wavefunctions of the $N\_N$-dimethyl-$p$-nitrosoaniline Ion States of $N\_N$-dimethyl-$p$-nitrosoaniline Labeled According to Figure 1*

<table>
<thead>
<tr>
<th>state</th>
<th>energy, eV</th>
<th>intensity, %</th>
<th>wavefunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-1.56$</td>
<td>100</td>
<td>$(0.0,0) - 0.39887$</td>
</tr>
<tr>
<td>2</td>
<td>1.17</td>
<td>66.9</td>
<td>$(29,29) - 0.00175$</td>
</tr>
<tr>
<td>3</td>
<td>3.07</td>
<td>11.5</td>
<td>$(29,29) - 0.30835$</td>
</tr>
<tr>
<td>4</td>
<td>3.47</td>
<td>25.0</td>
<td>$(29,29) - 0.56203$</td>
</tr>
<tr>
<td>5</td>
<td>3.87</td>
<td>7.5</td>
<td>$(29,29) - 0.00941$</td>
</tr>
<tr>
<td>6</td>
<td>4.79</td>
<td>4.8</td>
<td>$(29,29) - 0.00098$</td>
</tr>
<tr>
<td>7</td>
<td>5.02</td>
<td>5.9</td>
<td>$(29,29) - 0.00104$</td>
</tr>
</tbody>
</table>

*The energies are given relative to the uncorelated core-ionized ground state (SCF) state. The wavefunctions are characterized by their CI coefficient 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 slash.

TABLE II. Overlap Integrals between the Ionic and Neutral Molecule SCF Determinants for $N\_N$-dimethyl-$p$-nitrosoaniline* 

<table>
<thead>
<tr>
<th>state</th>
<th>$N_N$-dimethyl-$p$-nitrosoaniline</th>
<th>$N_N$-dimethyl-$p$-nitrosoaniline</th>
<th>$N_N$-dimethyl-$p$-nitrosoaniline</th>
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<tr>
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<tr>
<td>7</td>
<td>$[0,0]$</td>
<td>$[0,0]$</td>
<td>$[0,0]$</td>
</tr>
</tbody>
</table>

*See footnote to Table I.

in Figure 3. The overlap between the ion configurations listed in Table I and the Koopmans' ion state created from the neutral ground state are given in Table II. The lowest energy core-hole state exhibits the highest intensity and is completely screened ($\Delta g = 1.10\text{e}$). The wavefunction component with the highest amplitude is the SCF core-hole ground state, where 83% of the screening charge is drawn from the oxygen atom and the aromatic ring system, while the remaining 17% is derived from the amino nitrogen. The intense satellite line at $-1.7\text{e}$ above the main line has $\approx 70\%$ the intensity of the main line and, as shown in Table I cannot be attributed to a particular excited valence electron configuration. Note that the configurations given account for only 75% of the final-state wavefunction. The one- and two-electron excitations between the HOMO and LUMO levels equally contribute 25% to the total wavefunction. A second intense satellite line is called at $4.0\text{e}$. Again the wavefunction is a mixture of several excited configurations. The charge distributions in these excited states are such that the hole screening is smaller by $0.06\text{e}$ and 0.04e, respectively, compared to the core-hole ground state. However, the screening contribution due to charge transfer from the amino nitrogen to the NO group has increased by 0.12e and 0.12e, respectively. Therefore, the satellite peaks are very slightly less screened than the lowest binding energy term. The magnitude of amino nitroso group charge-transfer screening, however, is larger. Figure 3 illustrates the effect: upon electronic excitation from orbitals 27 and 29 to the LUMO level, the occupation of the amino group is reduced, whereas the NO occupation increases.

Such intramolecular charge transfer is the origin of the differences between the calculated spectral functions of nitrobenzene and $N\_N$-dimethyl-$p$-nitrosoaniline. The $N\_N$-dimethyl-$p$-nitrosoaniline ground state screening charge amounts to 0.8e in nitrobenzene and is, therefore, about 20% smaller than in $N\_N$-dimethyl-$p$-nitrosoaniline. Table II shows that the overlap of the core-hole ground state with the Koopmans' configuration is only 91% that of nitrobenzene. Corresponding overlaps between the HOMO LUMO single and double excitations and the Koopmans' configuration, however, are increased by 135% and 200%, respectively, relative to nitrobenzene. Consequently, the satellite region close to the main line already carries $\approx 122\%$ of the intensity of the line at lowest binding energy. This satellite intensity is essentially contained in two major components (no. 2 and 4).

From these results the chemical shift between the amino and nitroso spectral functions can now be estimated. Molecular potential calculations indicate that $N\_N$-dimethyl-$p$-nitrosoaniline lies above the N\_N$-dimethyl-$p$-nitrosoaniline ionization by 2.53 eV, whereas the relaxation energy difference obtained via the intensity sum rule is 2.47 eV. These terms yield 0.06 eV for the final binding-energy difference. The $N\_N$-dimethyl-$p$-nitrosoaniline spectral function in Figure 1 has been shifted by 0.06 eV relative to the N\_N$-dimethyl-$p$-nitrosoaniline ionization. The spectral function analysis appears to reflect the essential features of the experimental spectrum, particularly that the N\_N$-dimethyl-$p$-nitrosoaniline core-hole ground state is buried under the intense main peak as suggested by the above qualitative considerations.

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Table III. Energies and Wavefunctions of the OIs Ion States of N,N-Dimethyl-p-nitrosoaniline

<table>
<thead>
<tr>
<th>state</th>
<th>energy, eV</th>
<th>intensity, %</th>
<th>wavefunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.88</td>
<td>100</td>
<td>0.94566 (0.0)</td>
</tr>
<tr>
<td>2</td>
<td>2.32</td>
<td>46.4</td>
<td>-0.76729 (0.29,30.30) + 0.14186 (29.29,30.30) -0.19548 (26.26,30.30) +...</td>
</tr>
<tr>
<td>3</td>
<td>4.89</td>
<td>14.5</td>
<td>0.70739 (0.26,30.30) + 0.42136 (0.29,32.20) -0.36640 (26.29,30.30) +...</td>
</tr>
<tr>
<td>4</td>
<td>6.52</td>
<td>12.6</td>
<td>0.40591 (0.29,32.30) - 0.48683 (0.28,31.0) - 0.30364 (29.29,30.30) + 0.30152 (28.29,30.31) + 0.36328 (0.26,32.20)</td>
</tr>
</tbody>
</table>

*See footnote to Table I.

Table IV. Overlap Integrals between the Ionic and Neutral Molecule SCF Determinants for OIs Ionization of N,N-Dimethyl-p-nitrosoaniline

-0.011(0,0) -0.05052 (0,29,30.30) -0.318240 (26,36,30.0) -0.02076 (28,32) 0.004459 (0.0) -0.306581 (26,32.20) 0.13816 (29.29,30.30) -0.098172 (26,30.30,31) 0.002215 (28.0,30.31)

*See footnote to Table I.

Chemical shift calculations on nitroso-substituted aromatic compounds have been previously reported. Batch and Donald,27 for example, calculate shifts for comparable systems that are much larger than presently found. The earlier work, however, did not consider shakeup contributions.25 Distefano et al.13 have calculated the shakeup spectrum of N,N-dimethyl-p-nitrosoaniline using CNDO/S wavefunctions and singly excited configurations to describe excited core-hole states. Although the CI expansion including doubly excited configurations yields energy and intensity distributions in better accord with experiment, the present interpretation as to the nature of the most intense shakeup line nevertheless parallels the original assignment given by Distefano and co-workers.13

Three peaks were again used to qualitatively assess the OIs shakeup structure of Figure 2. The two bands assigned to the shakeup region (3.3 eV) were given equal weight. The total shakeup intensity below 10 eV is twice that found in nitrosobenzene.21 It appears, however, that the relative OIs shakeup intensity below 10 eV in Figure 2 is twice that found in nitrosobenzene.21 Figure 2 compares the theoretical OIs spectral function with experiment, and Tables III and IV contain the information necessary to analyze the contributions. The ground state of the core-hole is essentially a pure SCF hole state (90%) and is considerably less screened than the Nls(NO) hole state (72% vs. 101%, respectively). This, however, favorably compares with the OIs core-hole ground-state screening calculated for nitrosobenzene (71%).25 Although intramolecular charge transfer from the amino nitrogen contributes ~0.1 eV to OIs core-hole screening, the aromatic ring contributes less than in nitrosobenzene. The most intense OIs satellite (3.54 eV) is predominately a HOMO-LUMO excitation involving charge transfer from the donor to the acceptor group. OIs shakeup states 3 and 4 are ill-defined in terms of group character due to strong configurations mixing. The computations suggest that 45% of the OIs ionization intensity below 10 eV is contained in the satellites, with the remaining 55% forming the "main" line. Experimentally, the reverse percentages are found. The theoretical excitation energies of 3.5 and 5.7 eV (obtained as the average of 4.9 and 6.52 eV), however, are in excellent agreement with experimental values of 3.3 and 5.9 eV.

At this point we compare the Nls and OIs spectral functions in the vapor phase with those in the condensed molecular solid.13,27 From the vapor to the solid, the OIs shakeup intensity decreases substantially, being 0.55:1 and 0.30:1 in the solid.13 This is similar to the situation in nitrosobenzene but in contrast to the situation in p-nitroaniline, where there is some increase in relative intensity. On the other hand there is an increase in the Nls shakeup relative intensity in going from the gas to the solid, the relative intensities being 2.67:1 and 0.89:1. This is in agreement with the total N structure is half of the overall Nls spectral function. Thus the shakeup intensity is almost double what it is in the gas. We have studied in detail in a previous paper the influence of the formation of a solid on the core-hole spectra of nitrosobenzene.25 It was important to realize that upon condensation dimers are formed by establishing a chemical bond between two NO nitrogen atoms of two nitrosobenzene molecules.28 We were able to show that the shakeup intensity depends on the strength of interaction between the NO groups within the dimer.25 Results on the dimer within the geometry derived from X-ray crystallographic data28 indicated a reduced shakeup intensity with respect to the gas phase. Thus the observations reported here are not surprising. Nitrosoaniline intermolecular interaction, however, possibly involves trans-dimer formation.27 This is in contrast to the cis-configured dimer formed on condensation of nitrosobenzene.28

Summary and Conclusions

Vapor-phase Nls and OIs core-hole spectra for N,N-dimethyl-p-nitrosoaniline were presented. Theoretical spectral functions within the CNDO/S framework were calculated and were in good agreement with experiment. This made possible a detailed interpretation of Nls chemical shifts and various shakeup contributions. Comparisons were made with corresponding studies on nitrosobenzene. The "unusual" shape of the Nls spectrum, previously noted for N,N-dimethyl-p-nitrosoaniline in the solid state, was interpreted in terms of intramolecular charge-transfer screening between the amino and nitro groups. The importance of nitrogen was emphasized in the resolution of relative Nls(NO) and Nls(N(CH3)2) contributions.

The vapor-phase spectra was compared to existing solid-state results. Considerable differences in intensities were noted and attributed to strong solid-state intermolecular pairing or dimer formation. A detailed experimental and computational study of N,N-dimethyl-p-nitrosoaniline solid-state structure and core-hole properties is planned in order to sort out the nature and magnitude of the intermolecular interactions.

Acknowledgment. The experimental gas-phase work was supported by the National Science Foundation Grant No. CHE-8319476 and by the Vanderbilt University Research Council and Natural Science Committee. H.J.F. thanks the "Fonds der Chemischen Industrie" for financial support and Prof. G. Hohleinicher for his continued interest in this work.


(47) See the work by Lüttke et al. mentioned in ref 28.