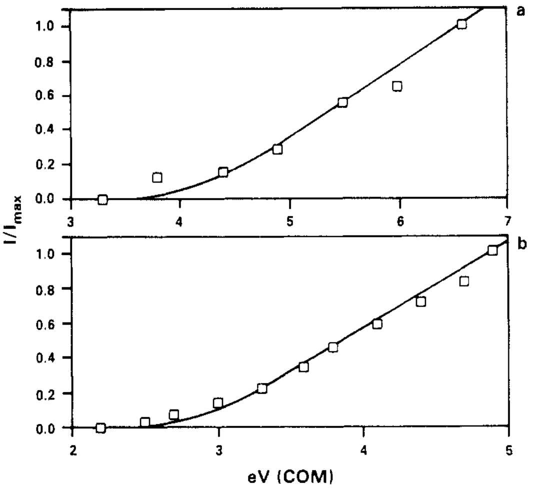


Figure 7. Ion yields of *m/z* 15 from (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ as a function of ion kinetic energy using NH_3 collision gas. The line represents the best fit to the theoretical doppler-broadened appearance curve (linear cross-sectional model).

due to the formation of NH_2CH_2OH (rather than HCOH) is greater than the gain in ΔH_r° due to the formation of NH_2CH_2OH (rather than CH_2O) for $CH_3OCH_2^+$. Here again the threshold ion kinetic energy can be used as an indicator of not only ion structure but also neutral structure.

Conclusion

Triple-quadrupole instruments are useful for the study of ion/molecule reactions and collisionally activated decompositions by "energy-resolved" experiments. Thermochemical limits obtained from these experiments can be used as an indicator of not only parent and of daughter ion structures but also neutral structure and even the reaction mechanism. Variation in the efficiency of the conversion of the translational energy into internal energy at the threshold apparently reflects the facility of the reaction mechanism, but it also hinders the direct interpretation of observed thresholds. Efficiencies in the literature, either stated or implied, range from approximately 15 to 25% conversion,[24] for a McLafferty rearrangement in 2-pentanone, to nearly 100% conversion,[19,21-23] for simple bond cleavages. Such a wide range of conversions would make it very difficult to determine the thermochemistry of an unknown reaction exactly, but instead an upper limit to the reaction enthalpy is produced. This will sometimes still provide the information needed to establish an ion structure, neutral structure, or reaction mechanism.

This study also illustrates the targeting of a specific characteristic of an ion structure when structural analysis is the purpose of the experiment. Holmes points out that this approach should be of the greatest use in the examination of ions of known structure.[35] It should also be pointed out, however, that the CAD product ions useful for the determination of unknown ion structures are still present in spectra obtained by using a reactive collision gas.[8] Since CAD products dominate the spectrum at high ion kinetic energy and exothermic ion/molecule reaction products dominate the spectrum at low ion kinetic energy, it should be possible to identify both CAD products and ion/molecule reaction products, as well as determine the thresholds for all endothermic processes, in a single energy-resolved ion/molecule study.

Registry No. $CH_3OCH_2^+$, 23653-97-6; CH_3CHOH^+, 17104-36-8; NH_3, 7664-41-7.

Vapor-Phase X-ray Core-Photoelectron Spectra of *N,N*-Dimethyl-*p*-nitrosoaniline. An Experimental and Theoretical Study

A. R. Slaughter,[†] **M. S. Banna,***[†] **R. W. Bigelow,**[‡] **H. Pulm,**[§⊥] **and H. J. Freund**[§]

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, the Xerox Webster Research Center, Webster, New York 14580, and the Institut für Physikalische und Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstrafe 3,8520 Erlangen, FRG.

Received August 19, 1985

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[$N(CH_3)_2$] 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-

---

[†] Vanderbilt University.

[‡] Xerox Webster Research Center.

[§] Universität Erlangen-Nürnberg.

[⊥] Present address: Henkel and Cie, 4000 Düsseldorf, FRG.

(1) Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S. E.; Lindgren, I.; Lindberg, B. *Nova Acta Regiae Soc. Sci. Ups.* **1967**, *20*, 1.

(2) Pignataro, S.; Distefano, G. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 171-182.

(3) Pignataro, S.; Dimarino, R.; Distefano, G. *J. Electron Spectrosc. Relat.* Phenom. **1974**, *4*, 90-92.

(4) Pignataro, S.; Distefano, G. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1975**, *30*, 815-820.

(5) Distefano, G.; Jones, D.; Modelli, A.; Pignataro, S. *Phys. Scr.* **1977**, *16*, 373-377.

0002-7863/86/1508-1801$01.50/0

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(NO_2) and O1s satellite intensities are significantly enhanced. Specifically, the gas-phase N1s(NO_2) 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 ($\Delta E \sim$ 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.[22-25] 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-workers[26] recently noted, and subsequently rejected, the notion that the condensed-phase multipeak N1s(NO_2) 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 NB[25] produced gas–solid-state core-level spectral function shifts paralleling experiment. Dimer models were used to simulate the solid-state environment. Fundamental modifications 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*-nitrosoaniline for comparison with existing condensed-phase results.[13,27] *N*,*N*-dimethyl-*p*-nitrosoaniline is particularly well suited to address the origin of vapor–condensed-phase spectral differences observed in donor/acceptor substituted aromatic systems. The nitrosobenzene

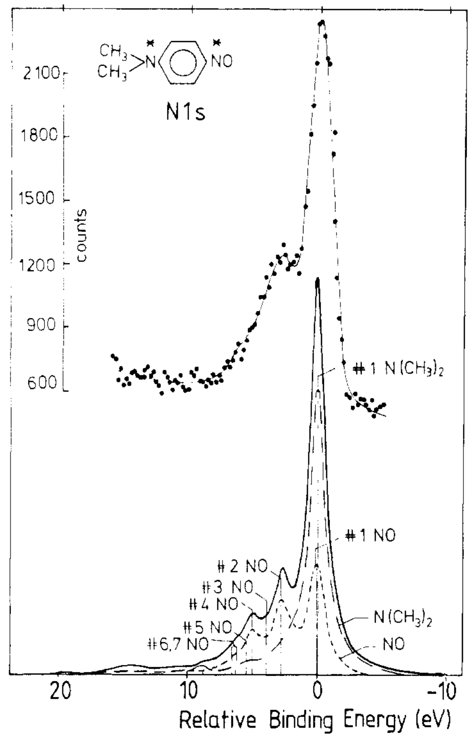


Figure 1. Comparison of the N1s core-hole spectrum of gaseous *N*,*N*-dimethyl-*p*-nitrosoaniline with the results of CNDO/S-CI calculations. The broken lines correpond to the theoretical spectral functions arising from N1s(NO) and N1s[$N(CH_3)_2$] ionization. The calculated intensities (certain states are labeled for discussion) are convoluted by a Lorentzian of half-width 0.75 eV.

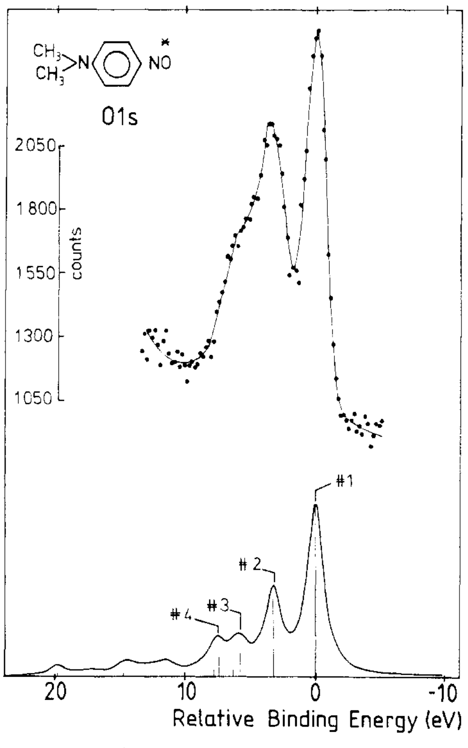


Figure 2. Comparison of the O1s core-hole spectrum of gaseous *N*,*N*-dimethyl-*p*-nitrosoaniline with the results of CNDO/S-CI calculations. States discussed in the text are labeled. The calculated intensities are convoluted by a Lorentzian of half-width 0.75 eV.

---

(6) Tsuchiya, S.; Seno, M. *Chem. Phys. Lett.* **1978**, *54*, 132–135.

(7) Nakagaki, R.; Frost, D. C.; McDowell, C. A. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *27*, 69–73.

(8) Katrib, A.; El-Rayyes, N. R. *Chem. Phys.* **1981**, *59*, 443–447.

(9) Bigelow, R. W.; Weagley, R. J.; Freund, H.-J. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *28*, 149–170.

(10) Bigelow, R. W.; Weagley, R. J.; Freund, H.-J. *Chem. Phys. Lett.* **1981**, *82*, 305–310.

(11) Sharma, J.; Garrett, W. L.; Owens, F. J.; Vogel, V. L. *J. Phys. Chem.* **1982**, *86*, 1657–1661.

(12) Colonna, F. P.; Distefano, G.; Guerra, M.; Jones, D. *J. Electron Spectrsoc. Relat. Phenom.* **1980**, *18*, 309–328.

(13) Distefano, G.; Guerra, M.; Jones, D.; Modelli, A.; Colonna, F. P. *Chem. Phys.* **1980**, *52*, 389–398.

(14) Distefano, G.; Guerra, M.; Colonna, F. P.; Jones, D.; Consiglio, G.; Spinelli, D. *Chem. Phys.* **1982**, *72*, 267–279.

(15) Guerra, M.; Jones, D.; Colonna, F. P.; Distefano, G.; Modelli, A. *Chem. Phys. Lett.* **1983**, *98*, 522–526.

(16) Distefano, G.; Guerra, M.; Jones, D.; Modelli, A. *Chem. Phys.* **1981**, *59*, 169–176.

(17) Domcke, W.; Cederbaum, L. S.; Schirmer, J.; von Niessen, W. *Phys. Rev. Lett* **1979**, *42*, 1237–1241; *Chem. Phys.* **1979**, *39*, 149–157.

(18) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; Von Niessen, W. *Phys. Scr.* **1980**, *21*, 481–491.

(19) Banna, M. S. *Chem. Phys.* **1980**, *45*, 383–385.

(20) Ågren, H.; Roos, B. O.; Bagus, P. S.; Gelius, U.; Malmquist, R.; Svensson, S.; Maripuu, R.; Siegbahn, K. *J. Chem. Phys.* **1982**, *77*, 3893–3901.

(21) Slaughter, A. R.; Banna, M. S.; McDowell, C. A. *Chem. Phys. Lett.* **1983**, *98*, 531–535.

(22) Freund, H.-J.; Slaughter, A. R.; Ballina, S. M.; Banna, M. S.; Bigelow, R. W.; Dick, B.; Lex, J.; Deger, H. *J. Chem. Phys.* **1984**, *81*, 2535–2555.

(23) Bigelow, R. W.; Freund, H.-J. *Chem. Phys. Lett.* **1981**, *77*, 261–266.

(24) Freund, H.-J.; Bigelow, R. W. *Chem. Phys.* **1981**, *55*, 407–427.

(25) Freund, H.-J.; Bigelow, R. W.; Borsch-Pulm, B.; Pulm, H. *Chem. Phys.* **1985**, *94*, 215–233.

(26) Owens, F. J.; Jayasuriya, K.; Abrahmsen, L.; Politzer, P. *Chem. Phys. Lett* **1985**, *116*, 434–438.

(27) Batich, C. D.; Donald, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 2758–2761.

moiety is known to form well-defined dimers upon condensation,[28] whereas dimethyl substitution of the amino nitrogen is expected to inhibit hydrogen bonding interactions. The hetereoatomic 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 N1s and O1s regions of gaseous *N*,*N*-dimethyl-*p*-nitrosoaniline with Al Kα X-rays (1486.582 eV[29]). 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. At present, photoelectrons emitted perpendicular to the X-ray beam are collected by the analyzer.

A commercial reagent-grade sample was used without further purification. The temperature needed to obtain sufficient vapor pressure was ~80 °C; this was achieved by using a resistively heated stainless steel oven. The N1s and O1s 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.[2-16,27] To obtain relative intensities and separations, Lorentzians or Gaussians 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 N1s region, since it was not possible to resolve the N1s (NO) peak from the N1s[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 semiemperical all-valence-electron closed-shell CNDO/S formalism[31,32] including up to doubly excited configurations[33] using the Pariser–Parr approximation[34] to the two-center repulsion integrals. Core-ionized species were treated within the equivalent-core approximation[35,36] 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 shake-up.[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[37] by projection of the correlated ion-state wavefunctions ($\Psi_{i,\text{rel}}$) onto that of the "frozen" ion state ($\Psi_{i,\text{frozen}}$) given in terms of the one-electron orbitals of the neutral system

$$I^i_{\text{rel}} \ \alpha\ |\langle \Psi^{\text{ion}}{}_{i,\text{rel}} \mid \Psi^{\text{ion}}{}_{i,\text{frozen}}\rangle|^2$$

Projections of the relaxed ion-state wavefunctions onto the correlated and uncorrelated initial state were performed to examine the importance of correlation contributions.[25,38]

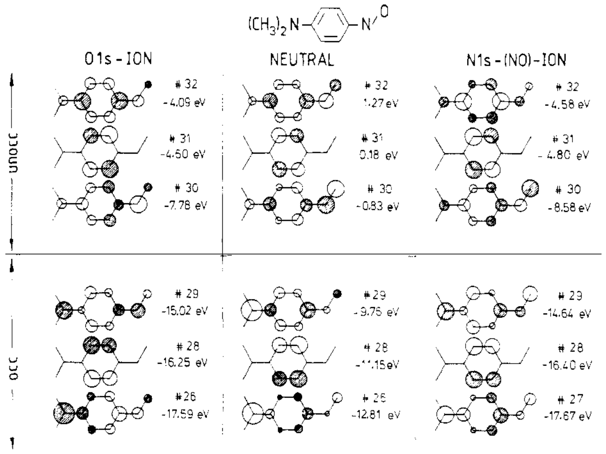


Figure 3. Localizations of the indicated *N*,*N*-dimethyl-*p*-nitrosoaniline orbitals as viewed from above the ring plane. The circles are approximately proportional to the LCAO coefficients.

Molecular coordinates used in the computations were calculated from bond lengths and bond angles given by Pople and Beveridge.[39]

Chemical shifts were obtained from neutral ground-state and relaxation contributions of the final ion state. Neutral ground-state contributions were calculated by using Gelius's model,[40] i e.

$$kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}}; \qquad k = 24.0$$

whereas relaxation contributions, E_{rel}, were calculated by using the sum rule[37,38,41]

$$E^j{}_{\text{rel}} = \sum_i (E^i{}_j - E^0{}_j) I^i{}_{\text{rel}}$$

$E^i{}_j$ and $E^0{}_j$ are the energies of all excited core-hole states, *i*, and the core-hole ground state, respectively.

Discussion

The proximity of the N1s peaks shown in Figure 1 is not surprising, although the two N1s ionizations in *p*-nitroaniline (PNA), for example, are separated by 5.2 eV.[20] An approximate upper limit to the splitting between the N1s peaks of *N*,*N*-dimethyl-*p*-nitrosoaniline can be obtained by comparing the N1s binding energy in nitrosobenzene (407.8 eV)[21] with that in *N*,*N*-dimethylaniline (405.1 eV).[42] This splitting of 2.7 eV is expected to be reduced due to the presence of the electron-donating [N$(CH_3)_2$] and electron-withdrawing (NO) groups on the same aromatic moiety. The decrease in splitting due to the second group can be estimated from the known decrease in the N1s(NO_2) binding energy of ~0.5 eV in going from nitrobenzene (411.7 eV)[43] to PNA (411.2 eV)[20] and from the increase in N1s(NH_2) binding energy in going from aniline (405.3 eV)[44] to PNA (406.0 eV).[20] The reduction in splitting, relative to N1s binding energies of the singly substituted systems, should be less than the 1.2 eV thus estimated, as NO_2 is more strongly electron withdrawing than NO. It is therefore likely that the N1s splitting in *N*,*N*-dimethyl-*p*-nitrosoaniline is less than 2.0 eV. This estimate favorably

---

(28) Dietrich, D. A.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1974**, *96*, 6372–6380. See also: Gowalock, B. G.; Luttke, W. *Q. Rev., Chem. Soc.* **1958**, *12*, 321. Luttke, W. *Z. Elektrochem.* **1957**, *61*, 302. Lüttke, W. *Z. Elektrochem.* **1957**, *61*, 976.

(29) Thomas, T. D.; Shaw, R. W.; Jr. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *5*, 1081–1094.

(30) Fadley, C. S. Ph.D. Thesis, Lawrence Berkeley Laboratory, Berkeley, CA, 1970.

(31) Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* **1968**, *48*, 1807–1813; **1968**, *48*, 4050–4055; **1968**, *49*, 1221–1229.

(32) Ellis, R. L.; Kuehnlenz, G.; Jaffe, H. H. *Theor. Chim. Acta* **1972**, *26*, 131–140.

(33) Dick, B.; Hohlneicher, G. *Theor. Chim. Acta* **1979**, *53*, 221–251.

(34) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767–776.

(35) Jolly, W. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1979**, *92*, 1863–1871.

(36) Davis, D. W.; Shirley, D. A. *Chem. Phys. Lett.* **1972**, *15*, 185.

(37) Manne, R.; Åberg, T. *Chem. Phys. Lett.* **1970**, *1*, 282–284.

(38) Freund, H.-J.; Pulm, H.; Dick, B.; Lange, R. *Chem. Phys.* **1983**, *81*, 99–112.

(39) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

(40) Gelius, U. *Phys. Scr.* **1974**, *9*, 133–147.

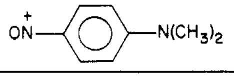
(41) Saddei, D.; Freund, H.-J.; Hohlneicher, G. *Chem. Phys. Lett.* **1979**, *68*, 222–224.

(42) Brown, R. S.; Tse, A. *J. Am. Chem. Soc.* **1980**, *102*, 5222–5226.

(43) Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Werme, L. O.; Manne, R.; Baer, Y. "ESCA Applied to Free Molecules"; North-Holland: Amsterdam, 1969.

(44) Ohta, T.; Fujikawa, T.; Kuroda, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2017–2024.

Table I. Energies and Wavefunctions of the N1s(NO) Ion States of *N*,*N*-Dimethyl-*p*-nitrosoaniline Labeled According to Figure 1[a]



state	energy, eV	intensity, %	wavefunction
1	−1.56	100	0.86064 $\langle 0,0 \Vert 0,0 \rangle$ − 0.39887 $\langle 29,29 \Vert 30,30 \rangle$ + ...
2	1.17	66.9	−0.50175 $\langle 0,29 \Vert 30,0 \rangle$ − 0.3437 $\langle 0,0 \Vert 0,0 \rangle$ −0.48228 $\langle 29,29 \Vert 30,30 \rangle$ + 0.38350 $\langle 0,27 \Vert 30,0 \rangle$ + ...
3	3.07	11.5	−0.76494 $\langle 0,29 \Vert 31,0 \rangle$ + 0.41958 $\langle 29,29 \Vert 30,31 \rangle$ + 0.27795 $\langle 27,29 \Vert 30,31 \rangle$ + ...
4	3.47	25.0	0.56203 $\langle 0,27 \Vert 30,0 \rangle$ + 0.50351 $\langle 27,29 \Vert 30,30 \rangle$ + 0.2563 $\langle 29,29 \vert 30,30 \rangle$ −0.24688 $\langle 0.29 \Vert 32,0 \rangle$ −0.2545 $\langle 0,21 \Vert 30,0 \rangle$ + ...
5	3.87	7.5	0.50941 $\langle 28,29 \Vert 30,31 \rangle$ − 0.31859 $\langle 28,29 \Vert 30,31 \rangle$ −0.29179 $\langle 29,29 \Vert 30,33 \rangle$ −0.3341 $\langle 0,29 \Vert 30,0 \rangle$ −0.28372 $\langle 0,27 \vert 30,0 \rangle$ + ...
6	4.79	4.8	0.50098 $\langle 0,29 \Vert 33,0 \rangle$ − 0.32196 $\langle 29,29 \Vert 30,32 \rangle$ −0.34939 $\langle 28,29 \Vert 30,31 \rangle$ + 0.25509 $\langle 29,29 \Vert 30,30 \rangle$ + ...
7	5.02	5.9	0.5034 $\langle 0,29 \Vert 31,0 \rangle$ − 0.40004 $\langle 0,29 \Vert 32,0 \rangle$ + 0.33017 $\langle 29,29 \Vert 30,30 \rangle$ − 0.20018 $\langle 0,29 \Vert 30,0 \rangle$ + ...

[a] The energies are given relative to the uncorrelated core-ionized ground (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.

compares to the observed decrease in N1s splitting on going from *N*,*N*-dimethylnitramine (5.1 eV) to *N*,*N*-dimethylnitrosoamine (1.3 eV).[45,46]

To resolve the experimental N1s splitting, it was decided to first fit a single peak to the most intense feature and two peaks to the shakeup region: one overlapping with the most intense band and the other, barely resolvable, lying on the high-binding-energy side. The approximate area ratios relative to the main peak are 0.35 ± 0.15:1 and 0.14 ± 0.07:1, respectively. The ratio of the sum of the shakeup features to the main peak is thus 0.5 ± 0.1:1. separations from the mean of the main peak are 2.9 ± 0.2 and 4.8 ± 0.5 eV. A more meaningful ratio, of course, is that of the shakeup intensities to the portion of the main line due to N1s(NO) ionization. Assuming that the total N1s(NO) intensity (shakeup plus main peak) is half the area of the entire N1s structure, ratios of the shakeup peaks to the main NO contribution of ~1.37:1 and ~0.55:1 are obtained from the values given above. The total shakeup intensity of 192 ± 45% relative to the NO peak is nearly 6 times that found in nitrosobenzene.[21]

Figure 1 compares the N1s spectral function calculation with experiment. The N1s [$N(CH_3)_2$] spectrum is essentially a single intense line. This line represents a hole state that is 63% screened. The screening charge is derived mainly from the carbon atoms directly bonded to the ionized nitrogen atom. The N1s(NO) spectrum, on the other hand, is a multiline spectrum including three relatively intense peaks. The seven strongest contributions are numbered. The energies and wavefunctions of these states are given in Table I. The numbers in brackets refer to the occupied (left of the vertical line) and unoccupied orbitals as shown 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 ($\Delta qe = 1.01e$). 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 ~2.7 eV above the main line has ~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 calcd. at 5.03 eV. 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*e* and 0.04*e*, 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 0.1*e* and 0.12*e*, or 29% and 30%, 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.

Table II. Overlap Integrals between the Ionic and Neutral Molecule SCF Determinants for N1s(NO) Ionization of *N*,*N*-Dimethyl-*p*-nitrosoaniline[a]

$\langle 0,0 \Vert 0,0 \rangle$	0.713054
$\langle 0,29 \Vert 30,0 \rangle$	0.310715
$\langle 0,27 \Vert 30,0 \rangle$	0.069780
$\langle 0,29 \Vert 33,0 \rangle$	−0.002997
$\langle 0,29 \Vert 31,0 \rangle$	−0.007712
$\langle 0,29 \Vert 32,0 \rangle$	0.060252
$\langle 0,21 \Vert 30,0 \rangle$	−0.022869
$\langle 29,29 \Vert 30,30 \rangle$	0.135395
$\langle 29,29 \Vert 30,31 \rangle$	−0.003361
$\langle 27,29 \Vert 30,31 \rangle$	−0.0004176
$\langle 27,29 \Vert 30,30 \rangle$	0.030407
$\langle 29,29 \Vert 30,32 \rangle$	0.026255
$\langle 28,29 \Vert 30,31 \rangle$	0.006433
$\langle 29,29 \Vert 30,33 \rangle$	−0.001306

[a] See footnote to Table I.

Such intramolecular charge transfer is the origin of the differences between the calculated spectral functions of nitrosobenzene[25] and *N*,*N*-dimethyl-*p*-nitrosoaniline. The N1s(NO) ground state screening charge amounts to 0.8*e* in nitrosobenzene[25] 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 nitrosobenzene.[25] Corresponding overlaps between the HOMO LUMO single and double excitations and the Koopmans' configuration, however, are increased by 135% and 200%, respectively, relative to nitrosobenzene. Consequently, the satellite region close to the main line already carries ~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).

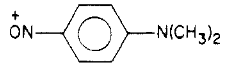
From these results the chemical shift between the amino and nitroso spectral functions can now be estimated. Molecular potential calculations[40] indicate that N1s(NO) ionization lies above the N1s[$N(CH_3)_2$] ionization by 2.53 eV, whereas the relaxation energy difference obtained via the intensity sum rule is 2.47 eV. These terms yield 0.06 eV for the final binding-energy difference. The N1s(NO) spectral function in Figure 1 has been shifted by 0.06 eV relative to the N1s amino group ionization. The spectral function analysis appears to reflect the essential features of the experimental spectrum, particularly that the N1s(NO) core-hole ground state is buried under the intense main peak as suggested by the above qualitative considerations.

---

(45) White, M. G.; Colton, R. J.; Lee, T. H.; Rabalais, J. W. *Chem. Phys.* **1975**, *8*, 391–398.

(46) Plaksin, P. M.; Sharma, J.; Bulusu, S.; Adams, G. F. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *6*, 429–450.

Table III. Energies and Wavefunctions of the O1s Ion States of *N*,*N*-Dimethyl-*p*-nitrosoaniline[a]



state	energy, eV	intensity, %	wavefunction
1	−0.88	100	0.94566 ⟨0,0‖0,0⟩ − 0.21124 ⟨29,29‖30,30⟩
2	2.32	46.4	− 0.76729 ⟨0,29‖30,0⟩ + 0.41486 ⟨29,29‖30,30⟩ − 0.19548 ⟨0,26‖30,0⟩ + ...
3	4.89	14.5	− 0.70739 ⟨0,26‖30,0⟩ + 0.42136 ⟨0,29‖32,0⟩ − 0.36640 ⟨26,29‖30,30⟩ + ...
4	6.52	12.6	0.40591 ⟨0,29‖32,0⟩ − 0.44863 ⟨0,28‖31,0⟩ − 0.30364 ⟨29,29‖30,30⟩ + 0.30152 ⟨28,29‖30,31⟩ + 0.36328 ⟨0,26‖32,0⟩

[a] See footnote to Table I.

Table IV. Overlap Integrals between the Ionic and Neutral Molecule SCF Determinants for O1s Ionization of *N*,*N*-Dimethyl-*p*-nitroaniline[a]

⟨0,0‖0,0⟩	0.640521
⟨0,29‖30,0⟩	0.318240
⟨0,26‖30,0⟩	−0.197592
⟨0,29‖32,0⟩	−0.022076
⟨0,28‖31,0⟩	0.004459
⟨0,26‖32,0⟩	−0.036581
⟨29,29‖30,30⟩	0.158116
⟨26,29‖30,30⟩	−0.098172
⟨28,29‖30,31⟩	0.002216

[a] See footnote to Table I.

Chemical shift calculations on nitroso-substituted aromatic compounds have been previously reported. Batich 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.[27] 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 O1s shakeup structure of Figure 2. The two bands assigned to the shakeup region (3.3 ± 0.2 and 5.9 ± 0.2 eV) were given equal line widths. The area ratios relative to the main peak are 0.85 ± 0.10:1 and 0.40 ± 0.06:1. The total shakeup to main-peak intensity ratio is 1.28 ± 0.07:1. Note, however, that additional shakeup peaks are present at high binding energies, as indicated by the sloping background in Figure 2, and by the fact that shakeup at ∼12.5 eV has been observed in nitrosobenzene.[21] It appears, however, that the relative O1s shakeup intensity below ∼10 eV in Figure 2 is twice that found in nitrosobenzene.[21]

Figure 2 compares the theoretical O1s 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 N1s(NO) hole state (72% vs. 101%, respectively). This, however, favorably compares with the O1s core-hole ground-state screening calculated for nitrosobenzene (71%).[25] Although intramolecular charge transfer from the amino nitrogen contributes ∼0.1*e* to O1s core-hole screening, the aromatic ring contributes less than in nitrosobenzene. The most intense O1s satellite (3.54 eV) is predominately a HOMO–LUMO excitation involving charge transfer from the donor to the acceptor group. O1s 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 O1s 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 N1s and O1s spectral functions in the vapor phase with those in the condensed molecular solid.[13,27] From the vapor to the solid, the O1s 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 N1s shakeup relative intensity in going from the gas to the solid, the relative intensities being 2.67:1 and 0.89:1[13] in the solid, again assuming that the total NO structure is half of the overall N1s 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] To understand the difference between vapor- and solid-phase spectra,[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 data[28] 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.[47] This is in contrast to the cis-configured dimer formed on condensation of nitrosobenzene.[28]

Summary and Conclusions

Vapor-phase N1s and O1s core-hole spectra for *N*,*N*-dimethyl-*p*-nitrosoaniline were presented. Theoretical spectral functions within the CNDO/S-CI equivalent-core approximation were in good agreement with experiment. This made possible a detailed interpretation of N1s chemical shifts and various shakeup contributions. Comparisons were made with corresponding studies on nitrosobenzene. The "unusual" shape of the N1s 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 nitoso groups. The importance of relaxation was emphasized in the resolution of relative N1s(NO) and N1s[N(CH$_3$)$_2$] 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. Hohlneicher for his continued interest in this work.

Registry No. *N*,*N*-Dimethyl-*p*-nitrosoaniline, 138-89-6.

---

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