

INTENSE CORE-HOLE SATELLITE STRUCTURE IN AROMATIC DONOR/ACCEPTOR MOLECULES

R.W. BIGELOW, R.J. WEAGLEY

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

and

H.-J. FREUND

Lehrstuhl für Theoretische Chemie der Universität zu Köln, 5000 Cologne 41, West Germany

Received 4 May 1981

Broad peak structure observed in the N1s(NO₂), O1s(NO₂) and N1s[N(CH₃)₂] core-hole spectra of trans-4-dimethyl-amino-4'-nitrostilbene (DANS) in the condensed phase is attributed to intense shake-up satellites.

1. Introduction

There has been considerable interest in the literature concerning the origin of the multipeak structure associated with the core-hole spectra of aromatic donor/acceptor systems (D⁺-Ar-A⁻) [1-14]. The N1s(NO₂) level of *p*-nitroaniline (PNA), for example, was shown to exhibit a characteristic doublet structure of approximately equal intensity well separated from the apparently single component N1s(NH₂) emission occurring at lower binding energy [1-6]. Although early assignments attributed these features to radiation damage [1], numerous recent studies have interpreted such multipeak structure in terms of valence-level excitations accompanying creation of the core hole [2-14].

Based on the results of ab initio computations on PNA Domcke and co-workers [10,11] assigned the high binding energy peak of the solid state N1s(NO₂) doublet to the primary *N*-1 electron core-hole state ²Ψ(*k*), whereas the second lower binding energy peak was attributed to a superposition of the 2h-1p "singlet"- and "triplet"-coupled doublet shake-up states arising from the well-characterized amino→nitro group π*←π intramolecular charge-transfer excitation, ²Ψ_{ππ*}¹(*k*) and ²Ψ_{ππ*}³(*k*), respectively. In addition, Domcke and co-workers [10,11] pointed out the similarities between the origin of the multipeak structure in the core-hole spectra of PNA and the *dynamical*

screening of adsorbate core holes by charge transfer from the substrate leading to similar multipeak structure [15-23]. In the nomenclature of the adsorbate system it was argued that due primarily to selective coulombic interactions, response of the substrate valence electrons (localized in the amino group π orbital) toward an adsorbate core hole (*k*) was such that the previously unfilled adsorbate level (the π* orbital localized on the nitro group) was "pulled" below ²Ψ(*k*) resulting in a situation characterized as negative shake-up, i.e. ²Ψ_{ππ*}^{1,3}(*k*) lies below ²Ψ(*k*). However, several works have subsequently appeared which question that negative shake-up in PNA has been fully demonstrated [12-14].

The purpose of this letter is to present experimental and theoretical results on the core-hole spectra of trans-4-dimethylamino-4'-nitrostilbene (DANS), fig. 1, which strongly suggest a significant negative shake-up contribution to *both* O1s(NO₂) and N1s(NO₂) ionization in the solid. In addition, a broad peak structure previously only observed concomitant with ionization of an acceptor core level in D⁺-Ar-A⁻ systems is present in the N1s[N(CH₃)₂] DANS spectra. This broadening of the N1s amino spectra relative to PNA in the solid is interpreted in terms of shake-up arising from orbital mixing with levels of adjacent "neutral" molecules.

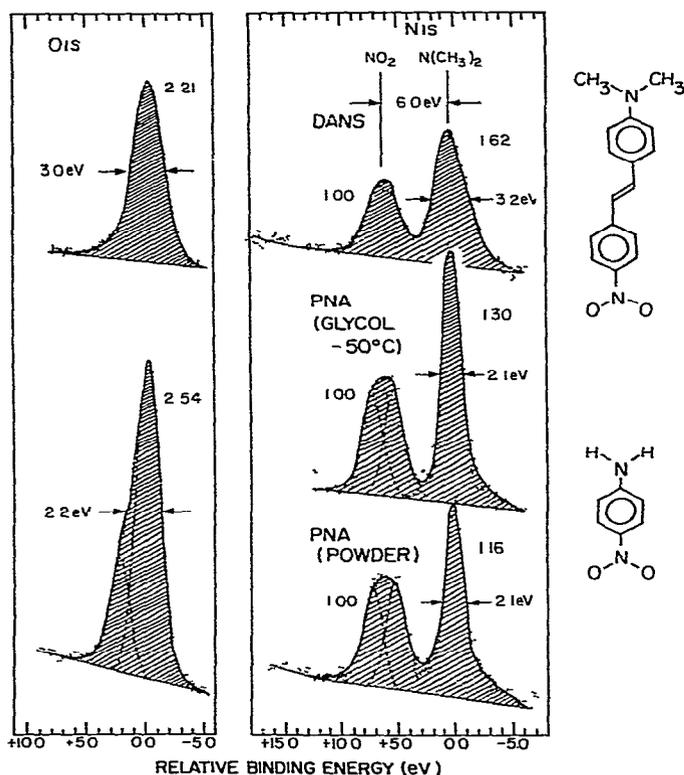


Fig. 1. The O1s and N1s XPS spectra of DANS and PNA. Peak areas relative to the broad N1s(NO₂) emission are indicated and suggest that the nitro group is oriented preferentially into the sample bulk. The N1s(NO₂) and O1s(NO₂) peaks of PNA are deconvoluted to indicate the multicomponent character.

2. Experimental

XPS measurements were conducted using an AEI ES200B photoelectron spectrometer (normal operating pressure 10^{-8} Torr) fitted with a low-temperature probe. Photoelectron spectra of DANS were accumulated using an unfiltered Mg K α source ($\hbar\omega = 1253.7$ eV), whereas spectra of PNA were obtained using an unfiltered Al K α source ($\hbar\omega = 1486.7$ eV). DANS (Eastman Organic Chemicals) was solvent cast from a saturated solution of chloroform directly onto the probe tip. Several preparations yielded comparable relative intensities and line widths. PNA (Aldrich Chemical Company) was (1) mounted in powder form directly onto the probe with double sided tape and (2) main-

tained on the probe tip in a saturated solution of glycol held at -50°C . In all cases the probe was rotated to maximize the signal intensity derived from the sample bulk so as to minimize possible effects due to a differential surface environment.

3. Computational

Equivalent-core computations [24,25] were performed within the closed-shell CNDO/S framework using singly excited configurations [26] to simulate perturbations to the valence orbital manifold of DANS by selected core holes by replacing the atom to be ionized (atomic number Z) by the atom following in the periodic table (atomic number $Z' = Z + 1$) and calculating the system as a closed-shell cation [9,13,14,25, 27,28]. It has been shown that the energies of the actual "singlet"- and "triplet"-coupled doublet $\pi^* \leftarrow \pi$ states, ${}^2\tilde{E}_{\pi\pi^*}^1(k)$ and ${}^2\tilde{E}_{\pi\pi^*}^3(k)$ respectively, can be adequately approximated from the corresponding excitation of singlet and triplet character in the closed-shell $Z + 1$ computation by equating the average configuration energies [13,14],

$${}^1,3\tilde{E}_{\pi\pi^*}^{\text{av}}(Z + 1) = {}^2,4\tilde{E}_{\pi\pi^*}^{\text{av}}(k), \quad (1)$$

where ${}^1,3\tilde{E}_{\pi\pi^*}^{\text{av}}(Z + 1)$ is obtained from the self-consistently calculated $Z + 1$ system and ${}^2,4\tilde{E}_{\pi\pi^*}^{\text{av}}(k)$ is obtained from an expansion of the multiplet wavefunction in terms of the neutral system. In the general case,

$${}^2\tilde{E}_{\pi\pi^*}^1(k) = {}^1,3\tilde{E}_{\pi\pi^*}^{\text{av}}(Z + 1) + K_{\pi\pi^*} + K_{\pi^*k} - \frac{1}{2}K_{\pi k} \quad (2)$$

and

$${}^2\tilde{E}_{\pi\pi^*}^3(k) = {}^1,3\tilde{E}_{\pi\pi^*}^{\text{av}}(Z + 1) + \frac{3}{2}K_{\pi k}, \quad (3)$$

where $K_{\pi\pi^*}$, K_{π^*k} and $K_{\pi k}$ are exchange integrals between valence levels, and the indicated valence level and the core hole, respectively. Due to spin selection rules the quartet state is not populated.

In the computation of excitation energies in the presence of the core hole for $D^+ - \text{Ar} - A^-$ structures it is advantageous to consider certain simplifying approximations based on the relative localization of the orbitals of interest, fig. 2 [13,14]. In the case of a core hole and π^* level localized on the nitro group, for example, we assume $K_{\pi^*k} \gg K_{\pi k}$ and $K_{\pi\pi^*}$ which

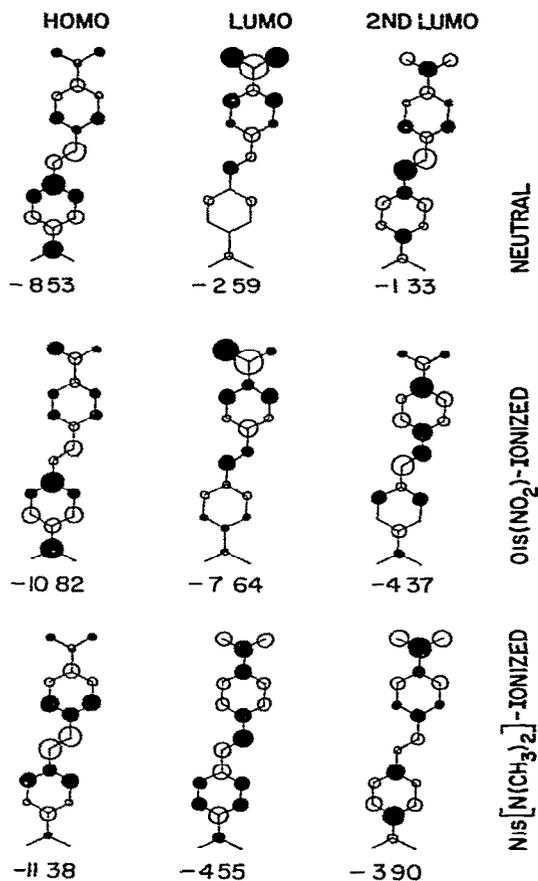


Fig. 2. A schematic view from above the molecular plane of the DANS orbitals of interest and their energy (eV). The orbital lobes are drawn proportional to the LCAO coefficients. Excitation in the neutral and O1s ionized species is to the LUMO levels, whereas the two excitations discussed in the text accompanying ionization of the donor nitrogen arise from excitation to the LUMO and second LUMO levels, respectively. The higher-lying virtual orbitals of the neutral and O1s ionized species are included merely to trace the nature of orbital mixing.

yields,

$${}^2\tilde{E}_{\pi\pi^*}^1(k) = {}^{1,3}\tilde{E}_{\pi\pi^*}^{av}(Z+1) + K_{\pi^*k} \quad (4)$$

and

$${}^2\tilde{E}_{\pi\pi^*}^3(k) = {}^{1,3}\tilde{E}_{\pi\pi^*}^{av}(Z+1), \quad (5)$$

whereas for a core hole and π level localized on the amino nitrogen $K_{\pi k} \gg K_{\pi^*k}$ and $K_{\pi\pi^*}$, and

$${}^2\tilde{E}_{\pi\pi^*}^1(k) = {}^{1,3}\tilde{E}_{\pi\pi^*}^{av}(Z+1) - \frac{1}{2}K_{\pi k} \quad (6)$$

and

$${}^2\tilde{E}_{\pi\pi^*}^3(k) = {}^{1,3}\tilde{E}_{\pi\pi^*}^{av}(Z+1) + \frac{3}{2}K_{\pi k}. \quad (7)$$

It is worth emphasizing that according to the above arguments the ordering of the doublet excitations is reversed on going from the acceptor to the donor core hole. However, for N1s[N(CH₃)₂] ionization (bottom panel fig. 2) the valence electron rearrangement is sufficiently large that the π level (HOMO) no longer has a significant localization on the amino nitrogen. In this case we approximate $K_{\pi^*k} \approx K_{\pi k} \approx 0$, and

$${}^2\tilde{E}_{\pi\pi^*}^1(k) = {}^{1,3}\tilde{E}_{\pi\pi^*}^{av}(Z+1) + K_{\pi\pi^*} \quad (8)$$

and

$${}^2\tilde{E}_{\pi\pi^*}^3(k) = {}^{1,3}\tilde{E}_{\pi\pi^*}^{av}(Z+1). \quad (9)$$

Since K_{π^*k} in eq. (4) is essentially an exchange interaction between an atomic 1s orbital and a valence π -orbital component of the π^* level and thus not directly calculated we must choose a suitable empirical value. It is expected that the experimentally observed splitting of the N1s ionization in the free NO molecule (1.2 eV) [29] is a reasonable approximation. $K_{\pi\pi^*}$ in eq. (8) is taken from our CNDO/S results ($K_{\pi\pi^*} = 0.40$ eV for N1s[N(CH₃)₂] ionization).

Shake-up intensities ${}^2I_{\pi\pi^*}^1(k)$ are calculated according to the relationships of Darko et al. [30] assuming only overlap between the virtual orbitals of interest in the $Z+1$ systems and the highest occupied molecular orbital in the neutral molecule. The expansion coefficients in the expressions of Darko et al. [30] reflecting direct coupling between ${}^2\Psi(k)$ and ${}^2\Psi_{\pi\pi^*}^1(k)$ and ${}^2\Psi_{\pi\pi^*}^3(k)$ cannot be extracted from our closed-shell method where only singly excited configurations are considered [13,14].

Atomic coordinates were derived for the isolated molecule from our earlier work on PNA [13,14] assuming only the trans configuration (planar π structure) and an alternating single-double-single bond linkage between aromatic chromophores of 1.46–1.34–1.46 Å, respectively.

4. Results and discussion

It is well known that DANS and PNA in the neutral states exhibit similar intramolecular $\pi^* \leftarrow \pi$ charge-transfer character, although the properties reflected

by such excitation are particularly enhanced in going from PNA to DANS [31,32]. Oudar [31] has compared the absorption spectrum of both systems and finds a red-shift in the long-wavelength excitation of ≈ 1.0 eV in going from PNA to DANS. This shift is reflected in our CNDO/S computations, and from a comparison of fig. 2 with our earlier work [13,14] can be attributed directly to the ≈ 1.0 eV shift to lower binding energy of the HOMO π level in going from PNA to DANS. This shift and the enormous increase in the polarizability and dipole moment upon excitation of DANS relative to PNA [31] strongly suggests the likelihood of greater core-hole induced valence-electron interactions in DANS.

Our computations yield ${}^2\tilde{E}_{\pi\pi^*}^3(k) = 0.35$ eV and ${}^2\tilde{E}_{\pi\pi^*}^1(k) = 1.55$ eV for O1s(NO₂) ionization of DANS. These values are ≈ 1.0 eV closer to the primary core hole than computed for PNA assuming the free-molecule environment [13,14]. In addition, ${}^2I_{\pi\pi^*}^1(k) = 30\%$ compared to 21.9% for O1s ionization of PNA. These trends clearly reflect the differences noted in the electronic structure of the neutral species.

Although we were unable to perform a computation for the N1s(NO₂) ionization which converged, a comparison with the results on PNA can nevertheless be achieved by assuming that the differences in doublet excitation energies for O1s and N1s(NO₂) ionization on going from PNA to DANS are similar. This approximation is clearly a lower limit due to the relative R^{-1} dependence of the core-hole-valence-electron Coulomb interaction. Therefore, for N1s(NO₂) ionization of DANS ${}^2\tilde{E}_{\pi\pi^*}^3(k) \leq -0.46$ eV and ${}^2\tilde{E}_{\pi\pi^*}^1(k) \leq 0.74$ eV.

The N1s[N(CH₃)₂] ionization of DANS leads to four states derived from excitation to the lowest two virtual orbitals, fig. 2, with energies ${}^2\tilde{E}_{\pi\pi^*}^1(k) = 5.72$, ${}^2\tilde{E}_{\pi\pi^*}^3(k) = 5.32$, ${}^2\tilde{E}_{\pi\pi^*}^1(k) = 3.32$ and ${}^2\tilde{E}_{\pi\pi^*}^3(k) = 2.92$ eV. Both "singlet"-coupled doublet excitations have an intensity of $\approx 3\%$. These relatively low-energy, high-intensity satellites indicate significant orbital mixing compared to the PNA results.

Perturbations to the O1s and N1s(NO₁) core-hole spectra of PNA on going from the free-molecule environment to the solid state have been clearly attributed to the sum of three components: (1) intermolecular orbital mixing between the LUMO level of the ion and the HOMO levels of the surrounding neutral molecules; (2) selective intermolecular coulombic interactions; and (3) enhanced direct coupling between ${}^2\Psi_{\pi\pi^*}^{1,3}(k)$

and ${}^2\Psi(k)$ as a result of the first two contributions which can be substantial for ${}^2\tilde{E}_{\pi\pi^*}^{1,3}(k) \approx {}^2\tilde{E}(k)$ [13,14]. However, due to prohibitive basis function requirements we were unable to approximate these interactions for DANS by simulating the solid-state environment with "ion-neutral" dimer pairing schemes such as in the case of PNA [13,14]. Therefore, we rely on comparisons with the PNA system to extrapolate the DANS free-molecule results to the solid state. In line with the similarities between the electronic structure of the two systems discussed above such a comparison should again provide a lower limit to the magnitude of the solid-state effects in DANS. For this purpose we briefly discuss donor and acceptor ionization separately.

It was shown that the O1s core-hole spectra of PNA was relatively unchanged on going from the vapor to the solid because the HOMO levels of the surrounding neutral molecules were shifted $\approx 3-4$ eV below the ion LUMO level by the field of the core hole [13,14]. On the other hand these levels were energetically close so as to promote orbital mixing for N1s(NO₂) ionization. This mixing was calculated to stabilize the doublet excitations by ≈ 0.5 eV relative to ${}^2\Psi(k)$. Assuming similar interactions, O1s ionization of DANS results in an interaction picture approximating the case of N1s(NO₂) ionization in PNA where the relevant levels are ≈ 2.0 eV apart. Therefore, taking -0.5 eV to represent the shift of the O1s doublet excitations relative to the primary core hole on going to the solid yields a spacing of ${}^2\Psi_{\pi\pi^*}^1(k) = 1.05$, ${}^2\Psi(k) = 0$ (by definition) and ${}^2\Psi_{\pi\pi^*}^3(k) = -0.15$ eV, an ordering clearly demonstrated for N1s(NO₂) ionization of PNA to lead to a double-peak structure [13,14]. Applying parallel arguments to N1s(NO₂) ionization in DANS we anticipate a solid-state doublet excitation shift ≥ -0.5 eV leading to a situation of "pronounced" negative shake-up; i.e. *both* ${}^2\Psi_{\pi\pi^*}^1(k)$ and ${}^2\Psi_{\pi\pi^*}^3(k)$ lie below the primary core-hole state ${}^2\Psi(k)$.

The orbital interaction scheme for N1s[N(CH₃)₂] ionization in the solid is outlined in fig. 3. Here mixing between the LUMO level of the ion and the LUMO levels of the neutral molecules, *and* between the HOMO level of the ion and the oxygen π -orbital lone pair of the neutral molecules appears energetically favorable. In the absence of methods with which to quantitatively obtain this shift we merely emphasize that orbital mixing is expected to displace the doublet state excita-

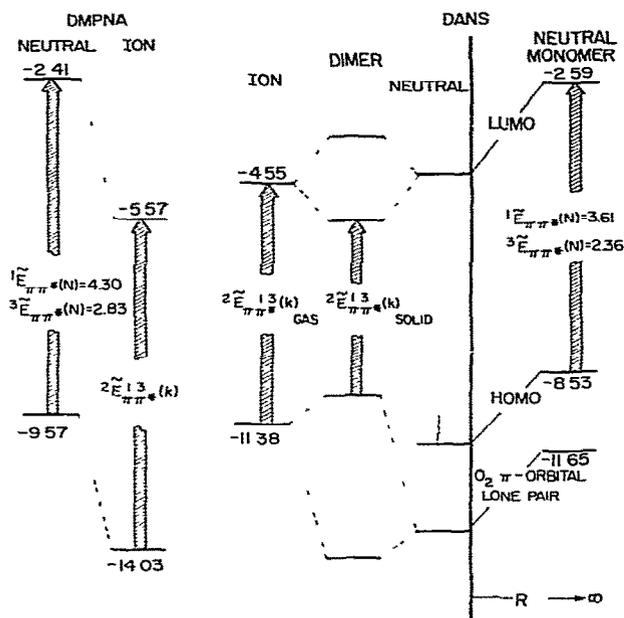


Fig. 3. A schematic representation of the gas to condensed phase orbital interaction (eV) for $N1s[N(CH_3)_2]$ ionization of DANS. For comparison the HOMO and LUMO levels of the neutral and $N1s[N(CH_3)_2]$ ionized species of *N,N*-dimethyl-*p*-nitroaniline (DMPNA) are given [13,14].

tion manifold to lower energy, thereby promoting direct coupling to the primary core hole. From the free-molecule calculations ${}^2\Psi_{\pi\pi^*}^1(k)$, and ${}^2\Psi_{\pi\pi^*}^3(k)$, derived from excitation between HOMO and LUMO levels, are the only states expected to significantly interact with ${}^2\Psi(k)$. We take the experimental results to indicate this solid-state interaction and satellite intensity enhancement. Although our results indicate a probable single-peak structure for the $N1s[N(CH_3)_2]$ vapor-phase ionization our current instrument configuration prohibited us from experimentally addressing this point.

In summary, our results indicate that under appropriate conditions excited-state configurations can occur which lie below the primary core-hole state, and that for a highly polarizable aromatic donor/acceptor molecule such as DANS intense shake-up satellite structure appears concomitant with ionization of both donor and acceptor.

References

- [1] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren and B. Lindberg, ESCA - Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, Nova Acta Regiae Soc. Sci. Upsaliensis, Ser. IV, Vol. 20 (1967).
- [2] S. Pignataro and G. Distefano, J. Electron Spectry. 2 (1973) 171.
- [3] S. Pignataro, R. DiMarino and G. Distefano, J. Electron Spectry. 4 (1974) 90.
- [4] S. Pignataro and G. Distefano, Z. Naturforsch. 30a (1975) 815.
- [5] G. Distefano, D. Jones, A. Modelli and S. Pignataro, Physica Scripta 16 (1977) 373.
- [6] S. Tsuchiya and M. Seno, Chem. Phys. Letters 54 (1978) 132.
- [7] A. Randino and F. Battaglia, J. Electron Spectry. 20 (1980) 327.
- [8] R. Nakagaki, D.C. Frost and C.A. McDowell, J. Electron Spectry. 19 (1980) 355.
- [9] G. Distefano, M. Guerra, D. Jones, A. Modelli and F.P. Colonna, Chem. Phys. 52 (1980) 389.
- [10] W. Domcke, L.S. Cederbaum, J. Schirmer and W. von Niessen, Phys. Rev. Letters 42 (1979) 1237; Chem. Phys. 39 (1979) 149.
- [11] W. Domcke, J. Schirmer and W. von Niessen, Physica Scripta 21 (1980) 481.
- [12] M.S. Banna, Chem. Phys. 45 (1980) 383.
- [13] R.W. Bigelow and H.-J. Freund, Chem. Phys. Letters 77 (1981) 261.
- [14] H.-J. Freund and R.W. Bigelow, Chem. Phys. 55 (1981) 407.
- [15] N.D. Lang and A.R. Williams, Phys. Rev. B16 (1977) 2408.
- [16] K. Schonhammer and O. Gunnarsson, Solid State Commun. 23 (1977) 691; 26 (1978) 399; Phys. Rev. B18 (1978) 6606; Z. Physik B30 (1978) 297.
- [17] O. Gunnarsson and K. Schönhammer, Solid State Commun. 26 (1978) 147; Phys. Rev. Letters 41 (1978) 1608; Surface Sci. 80 (1979) 471; Phys. Rev. B21 (1980) 5863.
- [18] S.S. Hussain and D.M. Newns, Solid State Commun. 25 (1978) 1049.
- [19] B. Gumhalter, Surface Sci. 80 (1979) 459.
- [20] R. Hoogewijs and J. Venrik, Solid State Commun. 31 (1979) 531.
- [21] D. Saddei, H.-J. Freund and G. Hohneicher, Surface Sci. 102 (1981) 359.
- [22] H.-J. Freund and E.W. Plummer, Phys. Rev. B, to be published.
- [23] H.-J. Freund, E.W. Plummer, W.R. Salaneck and R.W. Bigelow, J. Chem. Phys, submitted for publication.
- [24] W.L. Jolly and D.N. Hendrickson, J. Am. Chem. Soc. 92 (1970) 1863.
- [25] L.J. Aarons, M.F. Guest and I.H. Hillier, J. Chem. Soc. Faraday Trans. II 68 (1972) 1866.

- [26] J.E. Del Bene, H.H. Jaffé, R.L. Ellis and G. Kuehnlenz, QCPE 10 (1974) 174;
R.L. Ellis, G. Kuehnlenz and H.H. Jaffé, Theoret. Chim. Acta 26 (1972) 131.
- [27] D.T. Clark and A. Dilks, J. Polym. Sci. Polym. Chem. Ed. 15 (1977) 15.
- [28] T. Ohta, T. Fujikawa and H. Kuroda, Bull. Chem. Soc. Japan 48 (1975) 2017.
- [29] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne and Y. Baer, ESCA applied to free molecules (North-Holland, Amsterdam, 1969).
- [30] T. Darko, I.H. Hillier and J. Kendrick, Mol. Phys. 32 (1976) 33.
- [31] J.L. Oudar, J. Chem. Phys. 67 (1977) 446.
- [32] B.F. Levine and C.G. Bethea, J. Chem. Phys. 69 (1978) 5240.