Multi Peak ESCA Bands in Substituted Benzenes and Heterocyclic Compounds

S. Pignataro *

Istituto G. Ciamician, Università di Bologna, Via Selmi 2, 40126, Italy

and G. Distefano

Laboratorio dei Composti del Carbonio contenenti Eteroatomi e lolo Applicazioni del C.N.R.,
Via Tolara di Sotto 89, Ozzano E. (Bologna), Italy

(Z. Naturforsch. **30 a**, 815 – 820 [1975] ; received March 3, 1975)

The ESCA spectra of several substituted benzenes and heterocyclic compounds were obtained. Multi peak structures are observed in the various energy regions. The effects are generally interpreted as due to shake up phenomena involving intramolecular charge-transfer transitions between a "donor" and an "acceptor" group in the molecule. A quantitative model for such kind of phenomena is given. It rationalizes the fact that: 1) These shake up processes are, to a large extent, specific to the atoms of the acceptor groups; 2) the shake up energies found for the atoms of the donor part of the molecule (E_D) are generally higher than that (E_A) observed for the atoms pertaining to the acceptor group; when it is possible to correlate the shake up transitions to an U.V. one, the energy of the ultraviolet absorption transition seems generally intermediate between E_D and E_A. The analytical, spectroscopic and chemical importance of multi peak structures of ESCA bands is emphasized. In particular, the fact that it is not generally recognized that the shake up phenomena may cause strong broadening of the bands is criticized in connection with both the evaluation of ionization energies and the deconvolution procedures.

Introduction

Following our previous work on nitroanilines [1], chromium complexes [2] and pentatomic heterocycles [3], this paper presents some of the last results obtained in our laboratory on the multi peak structure of the ESCA bands of several organic compounds. These data show, once more, that the shake up phenomena [4] giving these structures should be observed [1] in almost any examined sample. The examples here reported, allow to discuss some aspect of the analytical, structural and spectroscopic importance of this phenomenon.

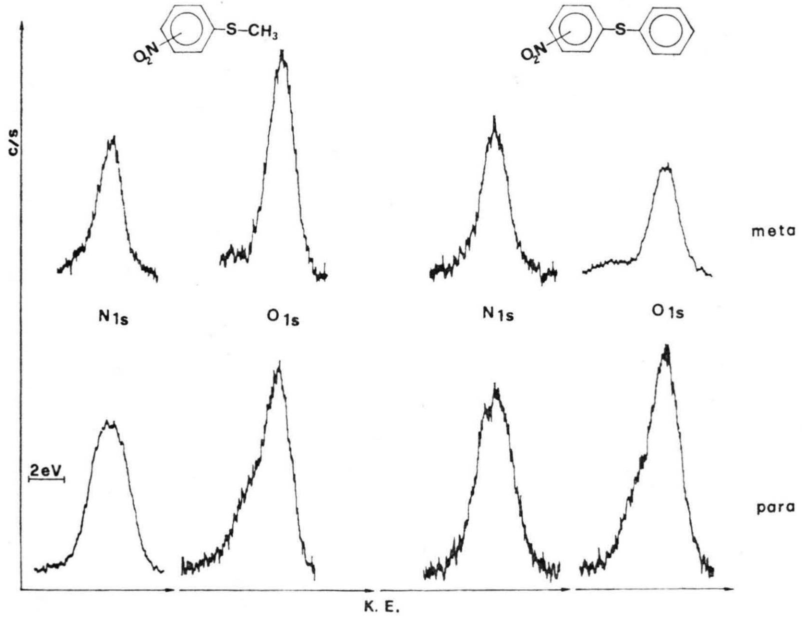


Fig. 1. N_{1s} and O_{1s} energy regions of the X rays photoelectron spectra of para and meta nitrothioanisoles and nitrodiphenylsulphides.

---

* Author to whom correspondence should be addressed. On leave to Institute of Physical Chemistry, University of Catania, Italy.

Substituted Benzenes

Figure 1 shows the X rays photoelectron spectra of meta and para nitrothioanisoles and nitrodiphenylsulphides. The meta derivatives are very similar to each other as far as the width of the N_{1s} and O_{1s} band is concerned. In particular the N_{1s} width is almost equal to that observed for the meta and para $NH_2-C_6H_4-SCH_3$ derivatives. The para derivatives also give rather similar N_{1s} and O_{1s} bands, but they are quite different from the corresponding meta which are clearly composite bands.

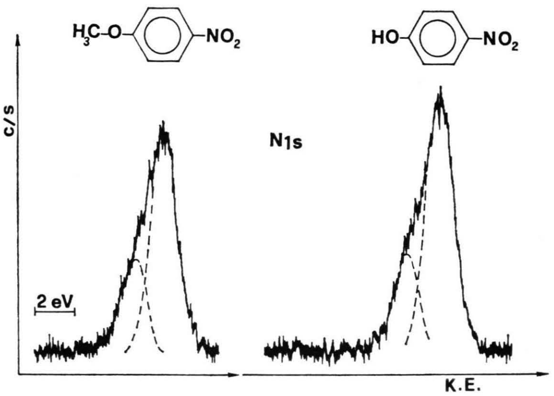


Fig. 2. N_{1s} energy region of the photoelectron spectra ($Mg_{K\alpha}$) of para metoxy and para hydroxy-nitrobenzenes.

A similar effect is also found for other nitroaromatic para substituted compounds. Figure 2 gives two more examples of the N_{1s} bands found in these compounds. Table 1 summarizes the most important [5]

X	N_{1s}	O_{1s}
NH_2	1.8	2.2
SCH_3	1.1	1.7
OCH_3	1.5	2.5
OH	1.7	2.5

Table 1. Shake up energies (eV) for some para substituted nitrobenzenes.

N_{1s} and O_{1s} shake up energies for the nitroderivatives here studied. The reported data show that the N_{1s} shake up energy is invariably lower than that found for the O_{1s} electrons. On the other hand the U.V. absorption energies [6-9] are higher than both O_{1s} and N_{1s} shake up energies. The effects are very similar to those previously reported for meta and para nitroanilines [1]. The only difference is that now they are of reduced importance, so that no clear doubling of the N_{1s} band is observed for the para compounds.

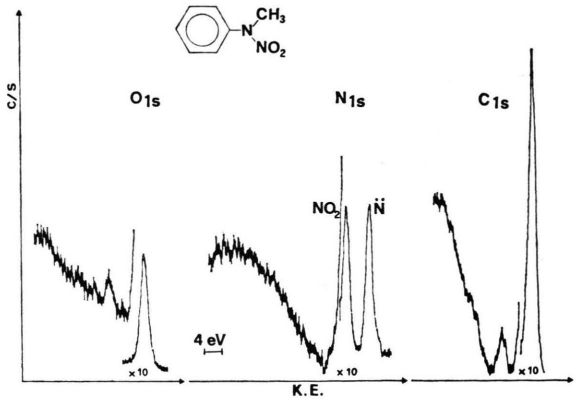


Fig. 3. C_{1s}, N_{1s} and O_{1s} energy regions of the photoelectron spectra of N-nitro, N′-methyl aniline ($Al_{K\alpha}$).

Figure 3 shows the ESCA spectrum of another aromatic nitroderivative. Only rather small C_{1s} and O_{1s} shake up peaks can be observed. It is interesting to note the almost equal intensity and shape of two N_{1s} bands which confirm that the effects found in the other nitroderivatives are originated by structural reasons.

Figure 4 reports another example of shake up peaks found in substituted benzenes. Here no strong shake up peak of energy comparable to that observed for

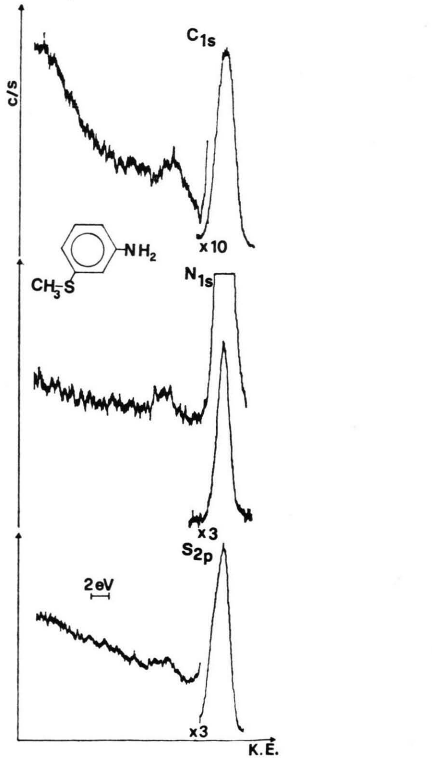
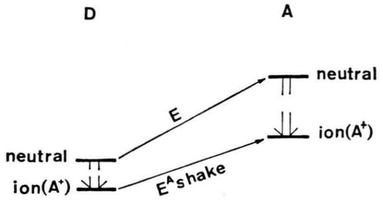


Fig. 4. $C1_1$, N_{1s} and S_{2p} energy regions of the photoelectron spectra of metaaminothioanisole ($Al_{K\alpha}$).

the nitrocompounds is observed (the FWHM of the N_{1s} band is 1.5 eV for example). Small peaks are instead observed for C_{1s}, N_{1s} and S_{2p} regions having energy of about 5.7, 6.5 and 6.0 eV respectively. The situation seems to be similar for the corresponding para compounds.

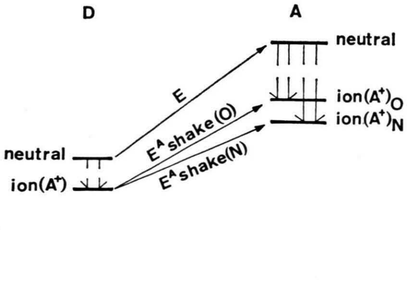
The results can be rationalized assuming the shake up transitions to involve a charge-transfer from a "donor" to an "acceptor" group of the molecules[10], in terms of the qualitative schemes 1 and 2. Let us assume to have a molecule in which there are two differently localized molecular orbitals: one filled (D) and the other (A) virtual. When the photoelectron process makes a positive hole on an atom of the part A of the molecule (Scheme 1), the molecular orbital mainly localized on A shrinks thoward the nuclei more than that mainly localized on D. So that the shake up energy necessary for the occurrence of the D→A charge transfer transition in the ion (E^{A}_{shake}) will be lower than the energy (E) required for the same transition in the neutral species.



For similar reasons it can be argued that when the positive hole concerns part D of the molecule, the energy for the corresponding C.T. process in the ion will be higher than in the neutral and sometimes not observed at all.

On the other hand, if the electronic transition does not significantly alter the charge density distribution, the E_{shake} is expected to be very similar to the U.V. absorption energy E.

The above naive picture seems to be supported by the shake up transitions observed in the N_{1s} and O_{1s} regions of the nitro derivatives. The situation here can be schematized as in Scheme 2, where D is a molecular orbital mainly localized on the benzene ring, and A is a M.O. mainly localized on the NO_2 group. As a first approximation we can assume that the M.O. D relaxes more or less of the same amount when an N_{1s} or O_{1s} electron is photoejected. But, the M.O. localized on the NO_2 group will shrink more for ejection of a N_{1s} with respect to an O_{1s} electron[1], since the nitrogen is more positive than the oxygen atoms already in the neutral species (the nitrogen atom has a formal positive charge). So that the ordering of the three relevant energies should be, as experimentally observed, $E_{shake}(N_{1s}) < E_{shake}(O_{1s}) < E$.



Pentatomic Heterocycles

The pentatomic heteroaromatic derivatives is another class of compounds which shows interesting multi peak bands.

The shake up band observed in the C_{1s} energy region of furan, pyrole and thiophen was assigned[3] to a shake up phenomenon involving a charge transfer process from the heteroatom to the carbon atoms of the rings. This was suggested[3] among others, from the similarity of the trend found for the C_{1s} shake up energies and the energy difference between the first two U.V. PES bands of the considered compounds. Recently, the photoelectron energy spectrum excited by U.V. radiation in gaseous phase was obtained for other two five membered heteroaromatic compounds, namely selenphen and tellurophen[11]. It was therefore possible to check the above hypothesis by studying the multi peak structure of the C_{1s} region of these two last compounds.

Figure 5 gives the C_{1s} photoelectron energy spectra of selenophen and tellurophen. As expected a small peak, whose E_{shake} is 5.0 and 4.1 eV respec-

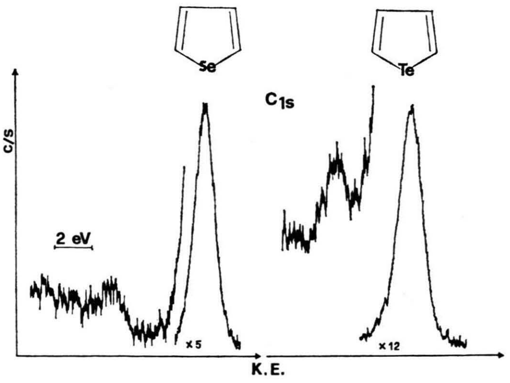


Fig. 5. C_{1s} energy regions of the photoelectron spectra of selenophen and tellurophen ($Mg_{K\alpha}$).

tively, accompanies the main C_{1s} line. If these small peaks are due to shake up processes involving a C.T. transition from the heteroatom to the carbon atoms, we would expect – for the reasons previously discussed – to find a correlation between E_{shake} and the energy difference between the π_3 and π_2 orbitals of these compounds[11]. The linearity of the trend (Fig. 6) is a clear support to the hypothesis made on the nature of the "extra" band in the C_{1s} energy region of the ESCA spectra of the considered compounds. It is interesting to note that for the tellurium derivative the reported $\pi_2 - \pi_3$ energy difference is negative according to the suggestion of an inversion of the last two occupied orbitals in tellurophen[12] with respect to the other congeners.

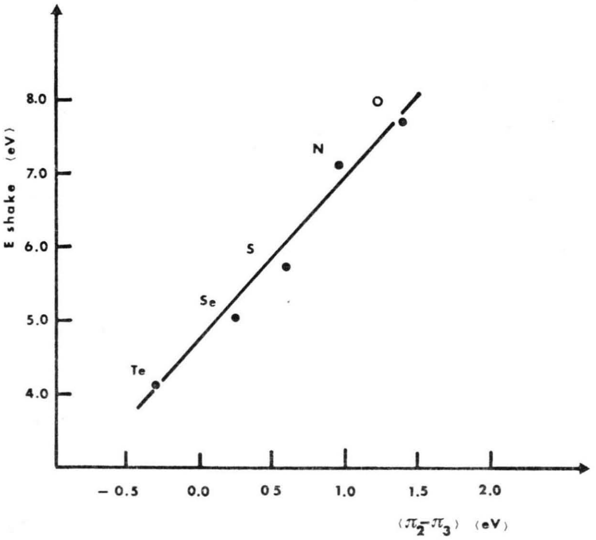


Fig. 6. Plot of the C_{1s} shake up energies vs. the energy difference of the first two U.V. PES bands for aromatic $(CH)_4X$ (X=O, N, S, Se and Te).

No shake up peaks at E_{shake} lower than 8.5 eV could be found in the present exp. cond. for Se_{3s}, Se_{3p}, Se_{3d}, Te_{3d} and Te_{4d} electrons in agreement with the fact that the molecular orbital of D type (see discussion of the substituted benzenes) are strongly localized on the heteroatom.

The nature of the D and A orbitals is probably also responsable of the trend observed for the relative intensity of the C_{1s} shake up peak with respect to the corresponding single excitation peak of the $(CH)_4X$ (O = 12%; NH = 6%; S = 5%; Se = 3.5%; Te = 2.5%). On going from O to Te, the π_2 orbital (D) should increase its "non bonding" heteroatom character, while the A orbital should not greatly change its butadiene characteristic[11].

Even if there is a lack of information on the symmetries of the corresponding ionic orbitals, we believe that the overlap between the D and A orbitals is probably decreasing in the same sense causing a decreasing intensity of the shake up peak.

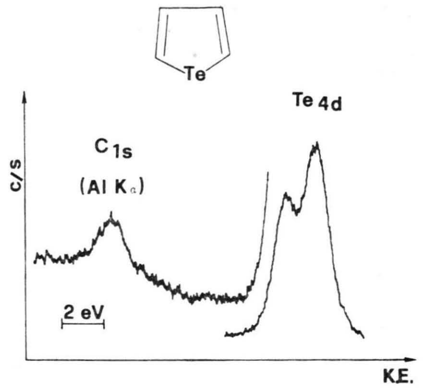


Fig. 7. Te_{4d} energy region of the photoelectron spectrum ($Mg_{K\alpha}$) of tellurophen. The C_{1s} satellite is originated from $Al_{K\alpha}$ radiation from the Aluminium window of the spectrometer.

Figure 7 reports the Te_{4d} region (spin-orbit splitting = 1.4 eV)[14] of tellurophen spectrum. The "extra" band on the low kinetic energy side of the Te_{4d} doublet is due to the C_{1s} electrons excited from $Al_{K\alpha}$ radiation coming from the Al window. This example shows the care needed in the interpretation of the "extra" bands observed.

Pyridine N-oxides

Figures 8 and 9 report the O_{1s} and N_{1s} energy regions of the ESCA spectra of the p-nitro and p-amino pyridine N-oxides respectively. As to the nitro derivative the assignements, reported in the

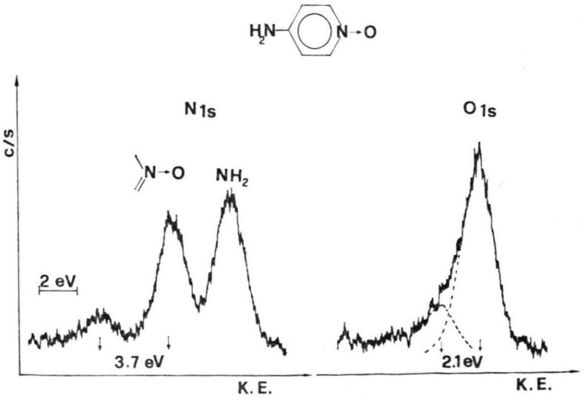


Fig. 8. N_{1s} ($Al_{K\alpha}$) and O_{1s} ($Mg_{K\alpha}$) energy regions of the X rays photoelectron spectra of the paranitropyridine N-oxide.

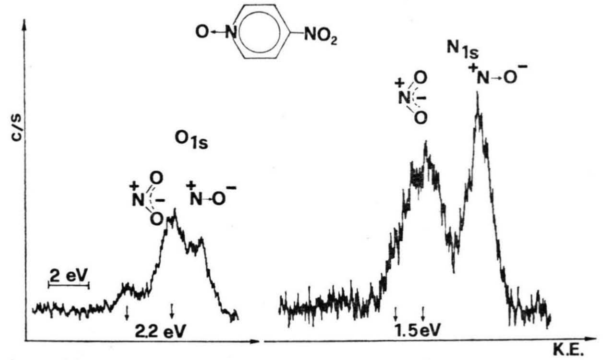


Fig. 9. N_{1s} and O_{1s} energy regions of the photoelectron spectra ($Al_{k\alpha}$) of the paraaminopyridine N-oxide.

figure, are done assuming a higher $\overset{+}{N}-\overset{-}{O}$ charge separation in N→O with respect to NO_2 groups.

The small peak at 2.2 eV (lower kinetic energy) from the $O_{1s}(NO_2)$ peak and the shoulder at about 1.5 eV from the $N_{1s}(NO_2)$ peak can than be assigned to shake up transition involving a charge-transfer from the ring to the NO_2 group. The observed values are very close to that obtained for the other nitroaromatic compounds.

Also in the amino derivative clear shake up structures are observed. A possible common interpretation of the small peak at about 3.7 eV and of the shoulder at about 2.1 eV from the main N_{1s} and O_{1s} peaks ($\overset{+}{N}\rightarrow\overset{-}{O}$) respectively, may be obtained by using again the same considerations reported previously for the substituted benzenes.

On these basis, the shake up transition appearing with higher energy on the N_{1s} region would suggest [15] a charge transfer from the ring to the O atom involving a "donor" orbital with an high parentage of the ring nitrogen.

Conclusions

The multi peak ESCA structure due to shake up transitions seems to be important for at least three reasons.

The first is an analytical reason. A look at the N_{1s} region allows for example to distinguish between the meta and the para nitroanilines or nitrothioanisoles.

Also the shake up structure of the heteroaromatic compounds permit to differentiate these compounds from the corresponding aliphatic compounds without recourse to the determination of core ionization energies [16].

The shake up structure gives also information on the electronic structure of the molecules. According to the proposed model the fact that a given shake up transition is observed for certain atoms of the molecule and not for others or that it is observed for the various atoms but with different energy, gives information on the electron density distribution of some M.O.'s in the neutral molecules. An example of this is given by the tellurophen case (see pentatomic heteroaromatic section).

The third reason of the importance of the ESCA multi peak structures comes out from the following considerations. Several examples of deconvolution of photoelectron bands can be found even in the recent literature. While people are generally aware that certain broadening of the bands may occur for example by solid state or charging up effects, it is not generally recognized that strong broadening of the bands may occur by shake up phenomena. A look at some of the examples here reported clearly shows that there are some cases in which, especially if low resolution spectra are considered, the shake up broadening strongly effects the ESCA data. If they are not correctly taken into account, not only the deconvolution procedures yield wrong results but also the absolute I.E. values of apparently unique peaks might be evaluated in a wrong way and any discussion based on chemical shifts should then give wrong conclusions. For example we can not correlate the I.E. of the N_{1s} electrons from meta nitrothioanisole with the I.E. value of the middle of the N_{1s} band of the corresponding para compound.

Experimental

The measurements were made on the AE I ES 100 spectrometer by using Alk_α or Mgk_α radiations as indicated in the figure legends.

The compounds were commercial samples. For other experimental conditions see Pignataro and Distefano.

Acknowledgement

One of us (S.P.) would like to thank C.N.R. (Rome) for financial support. The authors, would like to thank professors F. Fringuelli and A. Taticchi for the gift of a sample of tellurophen and selenophen.

[1] S. Pignataro and G. Distefano, J. Electron Spectr. Rel. Phen. **2**, 171 [1973].

[2] S. Pignataro, A. Foffani, and G. Distefano, Chem. Phys. Letters **20**, 350 [1973].

[3] S. Pignataro, R. Di Marino, G. Distefano, and A. Mangini, Chem. Phys. Letters **22**, 352 [1973].

[4] See for example K. Siegbahn, C. Nordling, G. Johanson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, ESCA Applied to Free Molecules, North-Holland Publ. Co., Amsterdam 1969, and references; M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. **170**, 37 [1968].

[5] Several small peaks are generally observed in every ESCA spectrum, however due to the difficulty of discriminating real effects from trivial ones (like decomposition phenomena, impurity of the samples or of the light source, background, etc.) the discussions in this paper will be restricted to the main features only.

[6] H. Suzuki, Electronic Absorption Spectra and Geometry of Organic Molecules, Academic Press, New York 1967.

[7] J. Degani, A. Mangini, A. Trombetti, and C. Zauli, Spectrochim. Acta **23 A**, 1351 [1967].

[8] R. Schaal and E. Peure, Bull. Soc. Chim. France **30**, 2638 [1963].

[9] R. Grinter and E. Heilbronner, Helv. Chimica Acta **45**, 2496 [1962].

[10] Excitation is generally accompanied by a redistribution of charge density and in this respect can be considered a charge-transfer process.

[11] G. Distefano, S. Pignataro, G. Innorta, F. Fringuelli, G. Marino, and A. Taticchi, Chem. Phys. Letters **22**, 132 [1973].

[12] This assignement[11] was recently supported also by the PES spectra[13] of the 2 CH$_3$ derivatives of O, S, Se and Te: the methyl substitution increases the separation of the first two PES bands for the O, S and Se derivatives, while decreases the separation of the first two PES bands for tellurophen.

[13] G. Distefano, F. Fringuelli, G. Marino, S. Pignataro, and A. Taticchi, unpublished data.

[14] Other spin-orbit splittings found during this study are: Te$_{3d}$ = 10.5 eV; Se$_{3p}$ = 5.8 eV; Se$_{3d}$ = 15.2 eV.

[15] We can not rule out, however, the possibility that the observed shape up bands would be due to entirely different transitions.

[16] The C$_{1s}$ I.E. of the (CH)$_4$X are invariably lower than that of the corresponding aliphatic compounds[3].