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# ESCA and UPS Spectra of Nitronaphthylamines

*Shake-up structures, relaxation effects and through-space interaction between the two substituents*

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## Abstract

*ESCA and UPS spectra of nitronaphthylamines: Shake-up structures, relaxation effects and through-space interaction between the two substituents.* G. Distefano, D. Jones, A. Modelli and S. Pignataro (Istituto di Chimica Fisica dell'Università, V. le A. Doria, Catania, Italy). *Physica Scripta (Sweden) 16, 373–377, 1977.*

The X-ray and UV photoelectron spectra of several nitronaphthylamine isomers are reported. In some cases, the nitro  $N_{1s}$  signal is accompanied by an intense satellite band 1.5–2.0 eV from the main photoline having 60–150% of its intensity; also in the corresponding  $O_{1s}$  energy region a satellite band is present having a larger energy separation from the main peak (2.0–2.3 eV) and smaller relative intensity ( $I_{sh}=10$ –30%). The difference between the ionization energy values of the nitro and amino  $N_{1s}$  signal ( $\Delta N_{1s}$ ) is found to follow the same trend found for the intensity of the satellite and  $\log \epsilon$ , the optical absorption coefficient of the HOMO–LUMO charge-transfer (CT) transition.

These satellites are ascribed to a shake-up process involving a CT transition from the naphthylamine part of the molecule towards a  $\pi^*$  MO localized on the nitro group on the basis of a simple model we have previously proposed for nitroanilines and other aromatic derivatives.

The trend of  $\Delta N_{1s}$  is thought to derive mainly from a greater "interatomic" valence band relaxation accompanying nitro  $N_{1s}$  ionization than amino  $N_{1s}$  ionization, rather than from variation of the ground state charges at the two nitrogen atoms.

The UPS spectra indicate that there is no sizeable variation of the ground state mesomeric interaction between the two substituents on changing the position of the nitro group, and suggest mutual interaction of the two substituents when they are adjacent.

## 1. Introduction

The suitability of the X-ray and UV photoelectron spectroscopic techniques for giving information on the electronic structures of molecular systems is well known. More recently it has been shown that multi-peak features of the X-ray photoelectron (ESCA) spectra, the so-called "shake-up" structures on the high binding energy side of the main photoline, can be related to the ground and excited state electronic configurations of the samples under investigation. Most of the work on such shake-up satellites has been recently reviewed by Brisk and Baker [1]. Since then, many other papers on the subject have appeared in the literature (see for example [2–15]) mainly dealing with very small molecules or metal complexes. We have recently discussed [16] the low-energy shake-up transitions in the ESCA spectra of several substituted aromatic molecules. As an extension of this work, in the present paper we report on the X-ray and UV photoelectron spectra of several nitronaphthylamine isomers, attempting to relate the ionization energies (I.E.) or their differences and ESCA shake-up data with differences in the electronic structure and conformation of these compounds, and also to correlate our results with those obtained from other physico-chemical properties. In particular, according to Pearson [17], the ground state

mesomeric interaction between the two functional groups may be related to the extinction coefficient of the band, in the electronic spectra, ascribed to a charge-transfer (CT) transition towards the vacant  $\pi^*NO_2MO$ ; Richard and Walker [18] related large interaction (dipole) moments to significant contributions from quinonoidal forms to the ground state configuration even in a non-interacting solvent; while, from  $pK_a$  measurements, Bryson concluded [19] that such conjugation is probably of limited significance in the acid–base reaction.

## 2. Experimental

All the compounds were obtained, commercially, being recrystallized before use.

The XPS results were obtained with an AEI ES200B electron spectrometer, using Al  $K_{\alpha}$  or Mg  $K_{\alpha}$  radiations, by subliming the samples *in vacuo* into a cooled gold surface before and during the measurements. The calibration of the amino group  $N_{1s}$  energy values against the  $Au_{4f7/2}$  line was carried out with very thin layers of sample on the gold surface ( $Au_{4f}$  signal approx. 10 times greater than that of  $N_{1s}$ ) to minimize charging effects. The reproducibility of the ESCA I.E. values was  $\pm 0.1$  eV.

The UV photoelectron spectra were obtained using a Perkin-Elmer PS18 photoelectron spectrometer. The He I resonance line (584 Å) served as the ionization source. The spectra were calibrated against Ar and Xe lines. The reproducibility was  $\pm 0.05$  eV and the accuracy is estimated to be  $\pm 0.05$  or 0.1 eV according to the number of decimal digits reported in Table II.

## 3. Results and Discussion

### 3.1. ESCA spectra

The relevant data from the ESCA spectra of the nitronaphthylamines studied are reported in Table I (together with the values of  $\log \epsilon$  [17], the optical absorption coefficient), while the  $N_{1s}$  and  $O_{1s}$  regions of the spectra are reproduced in Figs. 1 and 2 for the X- $NO_2$ , 1-NH<sub>2</sub> and X- $NO_2$ , 2-NH<sub>2</sub> derivatives respectively.

We start the discussion with the 1-NH<sub>2</sub> series. The  $N_{1s}$  energy region of the ESCA spectra of the X-nitro-1-naphthylamines shows two peaks 5–6 eV apart which can be assigned to electrons coming from the amino (lower I.E.) and nitro group nitrogens, the amino  $N_{1s}$  band being in all cases the more intense and sharper one (see Fig. 1). In the spectrum of the 4- $NO_2$  derivatives, however, the nitro  $N_{1s}$  band is split in two components of similar intensity separated by approx. 1.9 eV; also in the  $O_{1s}$  region of the spectrum a satellite band is present (see Fig. 1) having an energy separation from the main peak of 2.3 eV.

Table I. Relevant data from the ESCA spectra and  $\log \epsilon$  values of nitronaphthylamines

	Shake-up $N_{1s}(NO_2)$			$\log \epsilon^c$	$\Delta O_{1s}/N_{1s}$ (NH <sub>2</sub> ) (eV)	Shake-up $O_{1s}$	
	$\Delta N_{1s}$ (eV)	Energy (eV)	$I_{sh}^b$ (%)			Energy (eV)	$I_{sh}^b$ (%)
4-NO <sub>2</sub> -1-NH <sub>2</sub>	5.3	1.9	110	4.25	133.2*	2.3 <sub>s</sub>	30
7-NO <sub>2</sub> -1-NH <sub>2</sub>	6.2 <sup>a</sup>			3.62	133.5 <sup>d</sup>		
5-NO <sub>2</sub> -1-NH <sub>2</sub>	6.6 <sup>a</sup>			3.34	134.5		
6-NO <sub>2</sub> -1-NH <sub>2</sub>	6.6 <sub>s</sub> <sup>a</sup>			3.35	134.8	2.3	10
8-NO <sub>2</sub> -1-NH <sub>2</sub>	6.8 <sup>a</sup>			3.21	135.1		
6-NO <sub>2</sub> -2-NH <sub>2</sub>	5.7	1.5	150	4.15	133.6	Broad band	
1-NO <sub>2</sub> -2-NH <sub>2</sub>	5.3	2.0	60	3.84	134.2	2.0	15
7-NO <sub>2</sub> -2-NH <sub>2</sub>	6.5 <sub>s</sub> <sup>a</sup>			3.04	134.9	2.2	10

<sup>a</sup> In these cases the shake-up peak is not resolved; consequently, these values may be too high by a few tenths of an electron volt.

<sup>b</sup> The intensity is referred to that of the main line.

<sup>c</sup> Extinction coefficient of the absorption band in ethanol from ref. [17].

<sup>d</sup> Uncertain value.

(\*) These figures are highly accurate *only* if considered in a relative way.

eV whose intensity is about 30% of the main peak. These energy and intensity patterns of the satellite peaks in the  $N_{1s}$  and  $O_{1s}$  energy regions are very similar to those observed in paranitroaniline [20]. By analogy with the spectra of nitroanilines [20, 21], the peaks at the lowest kinetic energy are assigned to a shake-up phenomenon involving a charge transfer transition towards a vacant  $\pi^*$  MO localized on the nitro group. Also in this case in fact, the corresponding UV-visible absorption spectrum shows a CT band at about 3 eV (with similar values for the other isomers) assigned to the HOMO- (a  $\pi$  MO delocalized on the naphthylamine part of the molecule, see below) -LUMO (a  $\pi^*$  MO localized on the nitro group [17]) transition.

In the spectra of the other isomers of X-nitro-1-aminonaphthalene investigated here, low-energy shake-up structures are not resolved from the main photo-ionization peaks, but a shoulder or an asymmetry is present in the  $O_{1s}$  lines, while clear evidence of asymmetry in the nitro  $N_{1s}$  lines is not observed probably because of the smaller energy separation between the main line and the satellite. In all the cases, however, the nitro  $N_{1s}$  line has lower peak height and larger FWHM than the amino  $N_{1s}$  line:<sup>1</sup> after the 4-nitro compound, the greatest divergence from equal peak shape and height was observed in the 7-nitro derivatives (see Fig. 1).

In Table I, the difference between the ionization energy values of the nitro and amino  $N_{1s}$  signals ( $\Delta N_{1s}$ ) are reported. The value of  $\Delta N_{1s}$  was found to increase in the order  $x=4 < 7 < 5 < 6 < 8$ .

From Table I it is also evident that  $\log \epsilon$  and  $\Delta N_{1s}$  vary in a parallel manner (in fact a good linear relationship exists between them). Given that  $\log \epsilon$  has been related [17] to the extent of ground state mesomeric interaction between the two substituents, it would apparently seem possible to relate the variation of the  $\Delta N_{1s}$  value to differences in the ground state charges of the two nitrogen atoms brought about by changing the position of the nitro group. However, from  $pK_a$  measurements, Bryson concluded [19] that such conjugation is probably of limited significance; the UPS spectra also indicate (see below) that there is no sizeable variation of the mesomeric interaction with the position of the  $NO_2$  group; thus this is an unlikely explanation. The variation in  $\Delta N_{1s}$  along the series (1.5 eV) is mainly caused by the variation of the nitro group  $N_{1s}$  I.E. values with a negligible

<sup>1</sup> A different vibrational structure of the two  $N_{1s}$  lines cannot be excluded [22, 23].

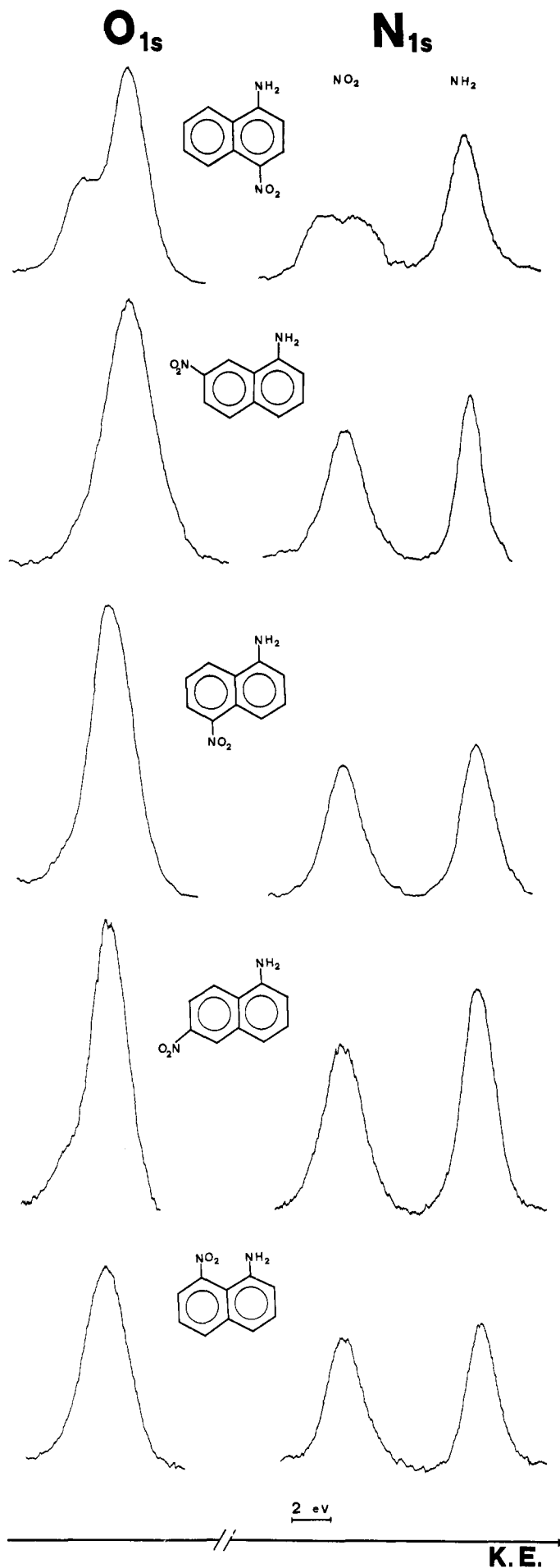


Fig. 1.  $O_{1s}$  and  $N_{1s}$  energy regions of the XPS spectra of some X-nitro-1-aminonaphthalenes.

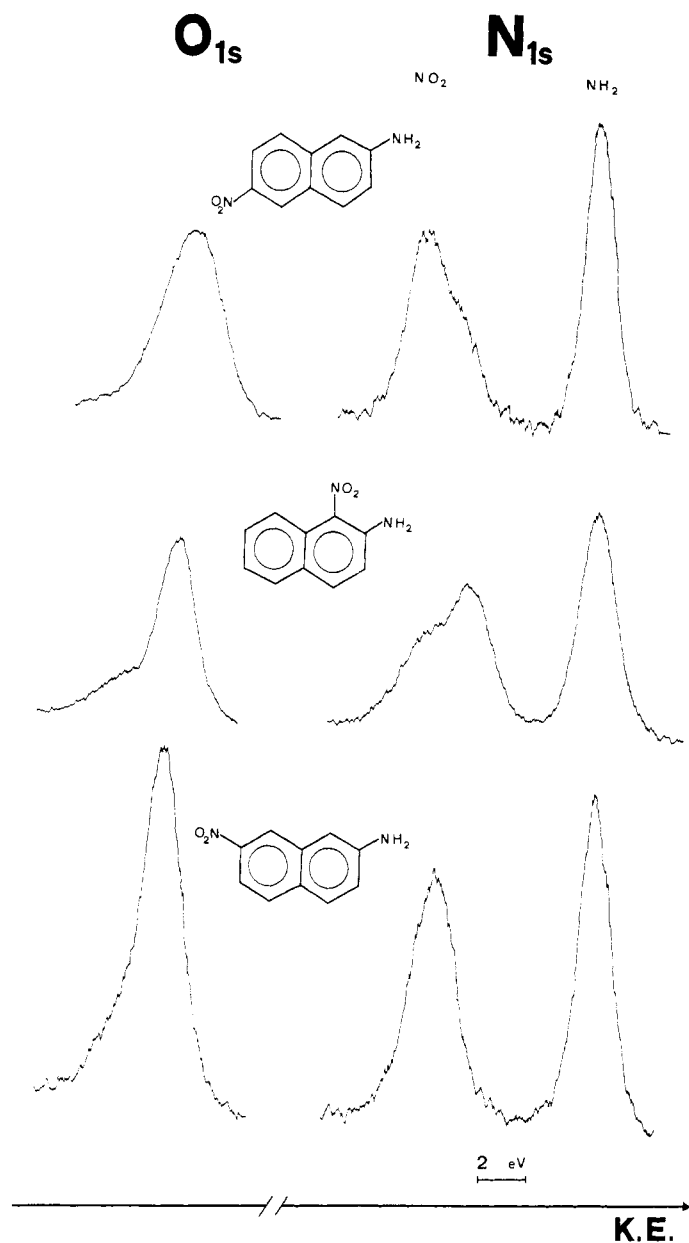


Fig. 2.  $O_{1s}$  and  $N_{1s}$  energy regions of the XPS spectra of some X-nitro-2-aminonaphthalenes.

contribution from the change in position of the amino group  $N_{1s}$  photoline, whose I.E. value is in fact constant (maximum deviation 0.2 eV) for all the derivatives. It has been pointed out [16, 24, 25] that the relaxation energy,  $E_r$ , accompanying ionization does not have a purely atomic character and consequently exerts a marked influence upon the chemical shift. We therefore assume that the variation of the nitro group  $N_{1s}$  I.E. value is mainly ascribable to larger changes in  $E_r$  accompanying nitro group  $N_{1s}$  photo-ionization.<sup>1</sup>

The correlation between the shake-up intensity and the value of  $\Delta N_{1s}$  accompanying the nitro group  $N_{1s}$  ionization is also to be noted: small  $\Delta N_{1s}$  [large  $E_r(\text{NO}_2)$ ] with intense shake-up for the 4-nitro derivative; moderate  $E_r$  and moderate shake-up intensity for the 7-nitro compound; and large almost constant  $\Delta N_{1s}$  and small shake-up intensity for the other three 1-NH<sub>2</sub>

<sup>1</sup> A variation in the ground state charge density of the carbon atoms with the position of the nitro group can concur with the variation in the nitro group  $N_{1s}$  I.E. value. Since this variation could be of the order of 0.1 eV for each carbon atom, it cannot be checked experimentally.

<sup>2</sup> As predicted by CNDO/2 calculations on related molecules [28].

derivatives. Such behaviour is expected because within the framework of the "sudden" approximation [26] the presence of intense shake-up satellites indicates [8, 15] a drastic electronic rearrangement (or relaxation effect) in the positive ion, relative to the neutral state. Thus the high intensity observed for satellite bands in some of the spectra of the present compounds (see also for the 2-NH<sub>2</sub> series later), confirms that in such cases differences in the relaxation accompanying the two  $N_{1s}$  ionizations play an important role in determining the  $\Delta N_{1s}$  value.

It is then possible to rationalize the observed multi-peak structure in the ESCA spectra of the X-nitro-1-aminonaphthalenes. To the extent that the ion state MOs differ from the ground state MOs the relative intensities of the satellites will increase and that of the primary photoline decrease [8, 11, 16, 20]. In particular, the relaxation of the valence MOs depends (i) on their localization at the ionized atom, (ii) on their possibility in the ionized molecule to interact with virtual orbitals mainly localized at the ionized atom, and (iii) on their polarizability [27]. Considering (i), the localization and the energy of the outermost filled MOs (see below), (ii) the localization of the LUMO at the NO<sub>2</sub> group (while the other low-lying  $\pi^*$  MOs are delocalized on the naphthylamine part of the molecule and therefore have small coefficients at the amino group), (iii) the small polarizability of the MOs localized on the nitro group due to the ground state partial positive charge at the nitrogen atom, the "interatomic" [25] valence band relaxation associated with the nitro  $N_{1s}$  ionization is expected to be much larger than in the amino case, thus explaining the much more intense shake-up structure of the nitro group  $N_{1s}$  lines relative to the corresponding amino  $N_{1s}$  lines. This conclusion is in agreement with the predictions of the simple model we have previously proposed [16, 20] for the interpretation of shake-up structures, which predicts a more intense shake-up associated with the photolines of the acceptor atoms in the CT process.

The difference between the  $N_{1s}$  and  $O_{1s}$  spectra of the nitro group can also be rationalized [8, 11, 16, 20]: the stabilization of the  $\pi^*$  NO<sub>2</sub> MO will be greater in the case of  $N_{1s}$  ionization than in the case of  $O_{1s}$  ionization because of the larger localization of that MO on the nitrogen atom than on the oxygen atoms,<sup>2</sup> thus explaining the differing energies of the satellites. Furthermore, because the core ionization at the nitrogen atom of this group is closer to the naphthalene nucleus, it will cause greater perturbation of the HOMO (along with other MO's localized on the naphthylamine part of the molecule) than will core ionization of the oxygen atom: the larger difference between the ground state MOs and the ions state MOs leads to a more intense shake-up structure in the case of  $N_{1s}$  ionization than  $O_{1s}$  ionization.

Given the relationship between shake-up intensity ( $I_{sh}$ ) and the relaxation energy ( $E_r$ ), which in this case largely determines

Table II. Valence band ionization energies of nitronaphthylamines

	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>
1-Naphthylamine <sup>a</sup>	7.46	8.66	9.26	10.49
4-NO <sub>2</sub> -1-NH <sub>2</sub>	8.05	9.33	9.63	10.5
7-NO <sub>2</sub> -1-NH <sub>2</sub>	8.00	9.30	9.80	10.9
5-NO <sub>2</sub> -1-NH <sub>2</sub>	8.00	9.27	9.68	10.9
8-NO <sub>2</sub> -1-NH <sub>2</sub>	8.00	9.35	9.68	11.0
2-Naphthylamine <sup>a</sup>	7.56	8.32	9.65	10.14
6-NO <sub>2</sub> -2-NH <sub>2</sub>	8.06	8.89	10.20	10.7
1-NO <sub>2</sub> -2-NH <sub>2</sub>	8.04	8.75	9.88	10.6
7-NO <sub>2</sub> -2-NH <sub>2</sub>	8.01	8.89	10.24	10.8

<sup>a</sup> From ref. [29].

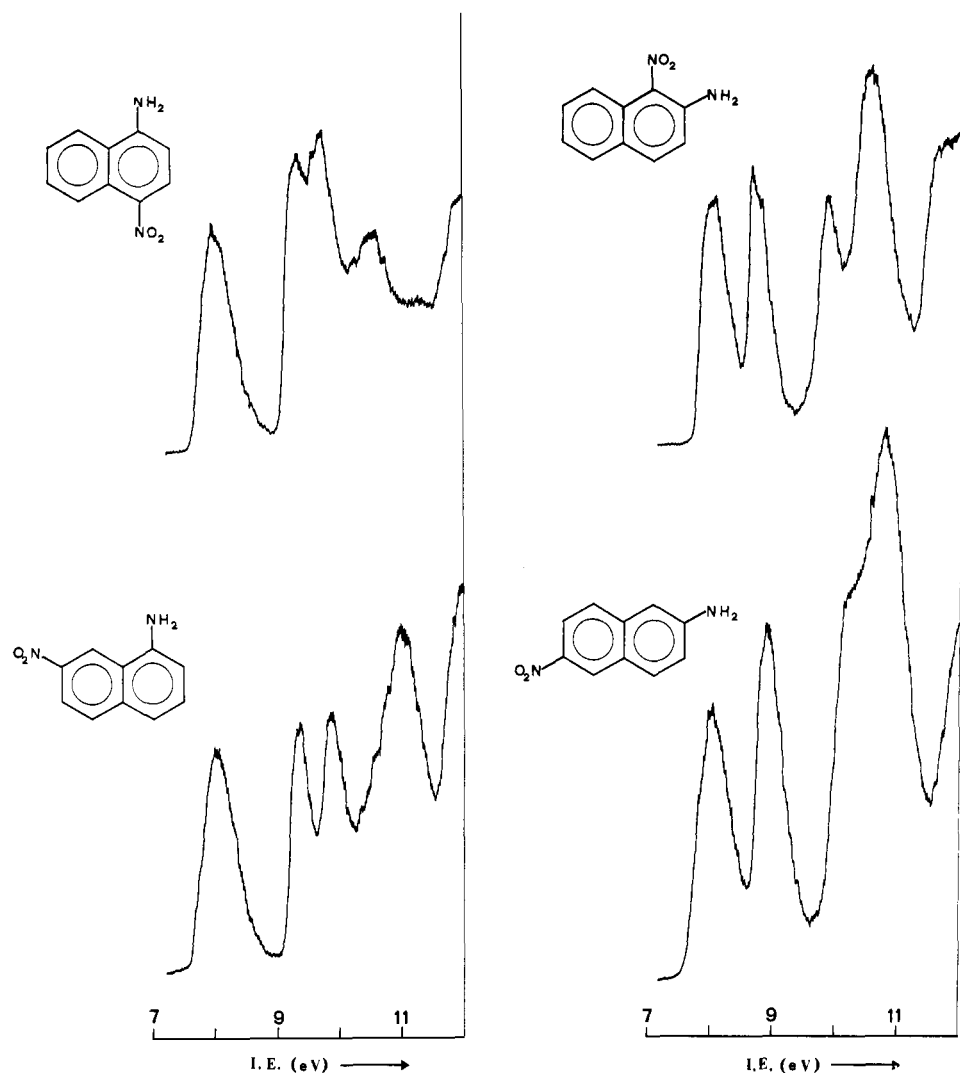


Fig. 3. Low IE region of the UPS spectra of some nitronaphthylamines.

the changes in  $\Delta N_{1s}$ , and the experimentally found linear correlation between  $\Delta N_{1s}$  and  $\log \epsilon$ ,  $I_{sh}$  and  $\log \epsilon$  should also be (linearly) related. This is because the intensity of the satellite bands depends upon the ordinary intensity determining dipole matrix element [8] which contains, *inter alia* a term proportional to the optical absorption intensity of the valence shell transition in the neutral molecule. This correlation, however, cannot be verified under present experimental conditions because the shake-up peak is not resolved in most of the spectra.

Regarding the X-NO<sub>2</sub>-2-NH<sub>2</sub> derivatives, the first remark to make is that the intensity of the shake-up transition accompanying nitro N<sub>1s</sub> ionization of the 6-NO<sub>2</sub>-2-NH<sub>2</sub> derivative, is about 150% of that of the main photoline (see Fig. 2).

The same comments made for the previous series hold also for the X-nitro-2-naphthylamines with the exception of the 1-NO<sub>2</sub>-2-NH<sub>2</sub> compound. In this compound the lowest  $\Delta N_{1s}$  value does not correspond to the most intense shake-up satellite but  $I_{sh}$  is still proportional to  $\log \epsilon$  (see Table I). The steric hindrance caused by the substituents being adjacent and a through space interaction might be responsible for this effect.

At first sight, the same effect should be present in the case of the 8-NO<sub>2</sub>-1-NH<sub>2</sub> derivative, but it clearly is not (see Table I). An explanation for this is proposed in the discussion of the UPS spectra.

### 3.2. UPS spectra

The UPS spectra of selected derivatives are shown in Fig. 3. Table II collects the first four I.E. values from seven nitro-

naphthylamines together with the corresponding values from 1- and 2-naphthylamine for comparison and assignment purposes. In the latter compounds, the first three bands have been assigned [29] to  $\pi$  MOs. On comparing the I.E. values of Table II, and considering that the MOs mainly localized on the NO<sub>2</sub> group appear in the spectra of benzene derivatives [28] at 10.6–11.3 eV, it is possible to relate the IE<sub>1–3</sub> values to the corresponding ones in the naphthylamines, and IE<sub>4</sub> to two ionization from the NO<sub>2</sub> group orbitals overlapping in some cases with IE<sub>4</sub>( $\pi$ ) of naphthylamines.

The effect of introducing the NO<sub>2</sub> group into the first three IE values of naphthylamines is remarkably constant in all the isomers for corresponding MOs (except IE<sub>2</sub> and IE<sub>3</sub> from the 1-NO<sub>2</sub>-2-NH<sub>2</sub> derivative) and therefore independent of the values of the wave function coefficients at the various ring positions. This finding is in agreement with the lack of (o-, m- and p-) positional dependence of the first three I.E. values in nitroanisoles and nitrophenols and is reproduced by CNDO/2 calculations on the latter two series [28]. These calculations also indicate that the first three  $\pi$  MOs have very low wave function coefficients at the nitro group. Assuming that the same holds good for nitronaphthylamines, the observed effect of the NO<sub>2</sub> group on the IE<sub>1–3</sub> values of naphthylamines is essentially inductive.

When IE<sub>4</sub> is considered, a remarkable destabilization (about 0.4 eV) is observed, in the 1-NH<sub>2</sub> series, for the 4-nitro derivative. It is ascribed to a relaxation accompanying this ionization given that IE<sub>1–3</sub> have the same values as in the other isomers.

The anomalous behaviour of the 1-nitro-2-amino derivative

(IE<sub>2</sub> and IE<sub>3</sub> destabilized with respect to the other isomers in the 2-NH<sub>2</sub> series) could be ascribed to steric hindrance (see also the ESCA results for this compound) which causes the two substituents to rotate, and a through-space interaction of the two substituents. In the absence of any special interaction, the rotation of the NH<sub>2</sub> group from the position of maximum interaction with the naphthalene nucleus should produce [29] an increase in the lowest I.E. values. However, an interaction between the oxygen lone pair "σ" MO<sup>1</sup> of the NO<sub>2</sub> group and the "π" MOs partially localized on the NH<sub>2</sub> group becomes possible. This interaction destabilizes the outer "π" MOs (mainly IE<sub>3</sub>) and stabilizes the "σ" MO of the nitro group. The observed values for IE<sub>1-3</sub> are in agreement with the presence of these two effects. The stabilization of the "σ" NO<sub>2</sub> MO is apparent from the shape of the fourth band which for the other isomers shows a shoulder on the low I.E. side which has been ascribed in similar compounds [28] to σ ionization, whereas, in the spectrum of the 1-NO<sub>2</sub>-2-NH<sub>2</sub> derivative, this shoulder is not present (see Fig. 3).

As far as the 8-NO<sub>2</sub>-1-NH<sub>2</sub> derivative is concerned, neither the UPS nor the XPS data show any sizeable effects of steric hindrance which is nevertheless present and is perhaps stronger than in the other isomers [17]. This fact could be explained by assuming (to our knowledge, there are no published structural data on these compounds) that the NH<sub>2</sub> group remains more or less in the plane of the molecule, while the NO<sub>2</sub> group is largely rotated out of the plane (about 90°) and therefore the relaxation from the naphthylamine part of the molecule during ionization of the NO<sub>2</sub> group is strongly reduced. That the distortion from the planarity in the 8-nitro-1-amino derivative is of a different nature than in the 1-nitro-2-amino derivative is also shown by pK<sub>a</sub> values and N-H infrared stretching frequencies [19]: whereas 8-NO<sub>2</sub>-1-NH<sub>2</sub> naphthalene has a pK<sub>a</sub> value similar to that of its non-hindered congeners, that of the 1-NO<sub>2</sub>-2-NH<sub>2</sub> derivative is much lower, in agreement with the retention in the former, and a strong reduction in the latter, of the NH<sub>2</sub> group conjugation with the naphthalene nucleus; in addition, the relative decrease in the N-H stretching frequencies is much greater in the 8-NO<sub>2</sub>-1-NH<sub>2</sub> than in the 1-NO<sub>2</sub>-2-NH<sub>2</sub> compound, in agreement with the conformation we propose.

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<sup>1</sup> In a non-planar molecule the σ and π labelling is incorrect. In the present case, however, this nomenclature is applied in order to make more clear the identity of the MOs considered.