Physica Scripta. Vol. 17, 50–63, 1987.

Dynamic effects in VUV- and XUV-Spectroscopy of Organic Molecular Solids

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Received August 4, 1986; accepted August 8, 1986

Abstract

Dynamic effects, i.e., shake up transitions in photoemission of non-polar, polar and, in particular, dipolar organic compounds are reviewed. Gas phase spectra are contrasted with solid phase spectra. For the non-polar molecules a one-to-one correspondence between the two phases is well documented. For polar and dipolar molecules, however, this one-to-one correspondence is lost, i.e., the dynamics of the hole creation process changes. It is shown that intermolecular screening becomes important. We develop simple physical criteria that allow to rationalize and predict under which conditions such effects are to be expected. In general it is concluded, that the interpretation of solid state spectra on the basis of calculations on the free molecule is not necessarily sound. We show, that even in cases where solid and gas phase spectra appear to be similar this similarity may be accidental and that it may be caused by particularly intermolecular interactions in the solid.

1. Introduction

Organic molecular solids offer important prospects in material science: Polymers have been formed from molecular solids, and organic conductors and superconductors can be designed for technical applications [1]. Langmuir–Blodgett films are ordered two-dimensional organic systes which can be used as models for biological membranes [2]. Energy transfer in such systems is a topic of current interest [2]. Langmuir–Blodgett films have recently been particularly attractive for developing new types of electronic devices [3]. For a long time organic materials have been used in non linear optics [4–7] and lithography [8]. While optical spectroscopy of organic molecular solids has a long tradition [9], systematic photoelectron spectroscopic studies have been undertaken mainly during the last 10–15 years [10–14]. Much progress has been made, and very recently the first energy band dispersion in a molecular solid has been observed [15]. In general the spectra of the organic molecular solids directly reflect the electronic structure of the isolated, gas phase molecule.

Therefore, the recent observation that certain organic compounds exhibit vapour phase spectra in the XPS regime considerably different from those observed for the condensed molecular solid has been of some interest [16–24]. The first example of such compounds for which the above mentioned anomaly was found is para-nitro-aniline (PNA) [25–27]. Compounds like PNA exhibit strong dynamic effects (multi-electron-shake-up-structure) accompaying particular ionizations in the system [16–40]. These dynamic effects change when the molecules are condensed to form a molecular solid [16–24].

The present paper is concerned with a discussion of such effects and the development of simple physical criteria that allow us to predict when such effects are to be expected. We start with a discussion of non-polar molecular solids and then turn to the above mentioned polar molecular solids.

2. Nonpolar molecular solids

Organic molecular solids exhibit a unique characteristic:

- The electronic structure of the isolated molecule in the gas phase is to a large extent preserved upon formation of the molecular solid.

This of course, is caused by the generally weak intermolecular van der Waals interaction between the molecular moieties in the crystal. Therefore, X-ray structure determination on molecular crystals is usually believed to provide us with the "gas-phase structure" of the molecule. A standard example is shown in Fig. 1; i.e., (solid) benzene. Since photoemission is one of the main probes to study the electronic structure of gas, liquids, and solids Fig. 1 shows a comparison between the photoelectron spectrum of benzene in the gas phase [14, 42] and in the solid [43]. There is a one-to-one correspondence between the photoelectron spectrum of the solid and the vapour. The main observations are:

- A shift of the ion states in the solid towards lower binding energies,
- A broadening of the photoemission peaks.

Theories have been developed [13, 44] that allow one to understand this shift via polarization of the surrounding molecules by the created hole localized on one moiety. The localization is due to the weak intermolecular interaction among the molecules in the crystal. The polarization of the surrounding molecules stabilizes the final ion state, and thus leads to a decrease in binding energy [13].

The situation is depicted schematically in Fig. 2. Both, the ground (N-electron system) and the ion (($N - 1$)-electron system) states of the solid are stabilized by, in general, different van der Waals interactions. This does not strongly affect the binding energy in comparison to the gas phase. However, the strong polarization is only effective in the ion state and leads to a shift of the binding energy. Salaneck [45] confirmed this hypothesis by observing a difference in the relaxation energies for hole states in the bulk and

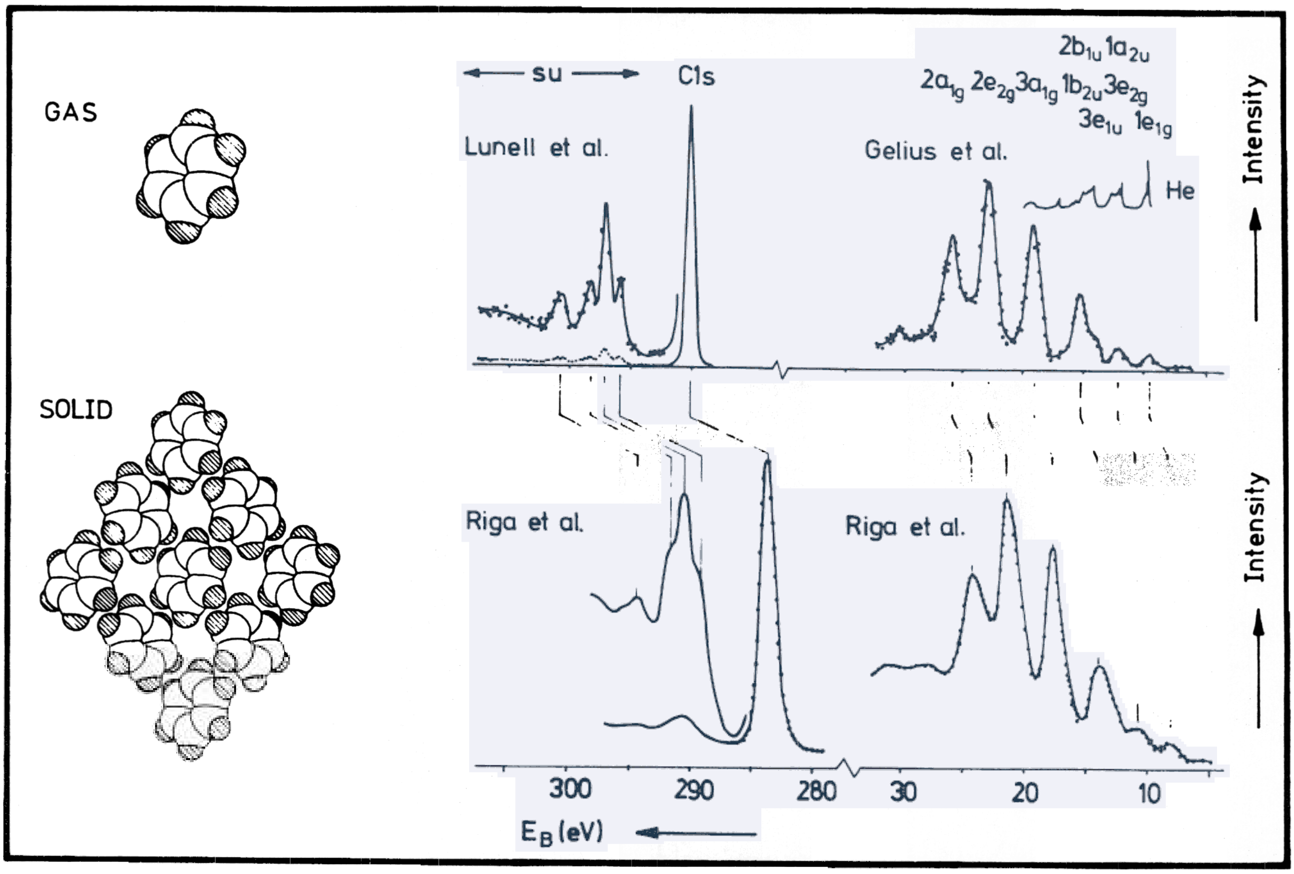


Fig. 1. Comparison of the valence and inner electron ionization spectra in the gas phase [41, 42] and the solid phase [43]. At the top an orbital assignment is given and corresponding ion states in the gas and the solid phase are connected. On the left, schematic representations of the molecular structure and its environment in the molecular solid are given.

on the surface of a molecular crystal: The surface relaxation is smaller, which is precisely what one would expect because the surface molecules are surrounded by only half as many polarizable neighbours than the bulk molecules. The rigidity of the binding energy shift for all valence ion states of about 2.0 eV (Fig. 1) is remarkable since in principle it could vary from one hole state to another. For core holes, for example, the corresponding extramolecular relaxation energy is much larger, i.e., 6.1 eV, which is believed to be due to the higher degree of localization of a core hole as compared to a valence hole. A recent analysis of Auger spectra of gas phase and condensed benzene arrives at similar conclusions [46].

It is quite evident that the core holes remain localized in the solid state. The local or extended nature of molecular ion-states in molecular solids is determined by a competition between fluctuation in the local site energies of these states (which tend to localize them) and the hopping probability for inter-site excitation transfer (which tend to delocalize them) [47]. These site fluctuation ingredients determine the observed larger line widths in the photoemission spectra of molecular solids, and also the temperature dependence of the line widths, which has been observed experimentally [48]. In the thinking about excitations in molecular solids it may cause conceptual difficulties to consider these excitations in terms of the traditional energy band theory of solids. Rather, such excitations should be regarded as localized entities which move through the solid via hopping.

The localized nature of the hole states reflects itself in the population of hole states that involve the excitation of more than one electron i.e., so called shake up states. Fig. 1, left hand side, shows the shake up spectrum accompanying the C1*s* electron ejection of gaseous and solid benzene. Shake up satellites are caused by excitations among the valence electrons in the presence of a hole, and are thus due to 2-hole-particle states (2h*p*). Their intensity is governed by the projection of the created 2h*p*-ion state onto the frozen hole state, which can be thought to be created through a sudden removal of an electron, fast enough that the remaining electrons cannot adjust to the change of the potential (see Appendix for details). The excitation energies of the shake up states relative to the intense "main" line as well as their relative intensities line up perfectly in the gas and the solid phase spectra (Fig. 1), indicating that the valence electron distribution in the C1*s*-hole-state of benzene is similar in the gas and the solid. In other words, the polarization stabilization of the ion embedded in a dielectric medium of polarizable neighbours acts in an average fashion on the valence electrons, and does not change the detailed electronic distribution. This is what one would expect for a van der Waals solid. The observability of these shake up processes has been used for some interesting analytical applications in polymer studies. Clark [14] and Dilks [49] have taken advantage of the fact that the benzene shake up is energetically clearly removed from the main line. Fig. 3 shows C1*s* spectra of polyethylene and of polystyrene as reported by Dilks [49]. The main lines of the aliphatic and the aromatic C1*s* ionizations almost coincide and thus do not allow clear separation of the two signals. However, the fact that the pendant group ionization is accompanied by a characteristic shake up transition, while the aliphatic backbone ionization is not [Fig. 3(a)] allows identification of the former.

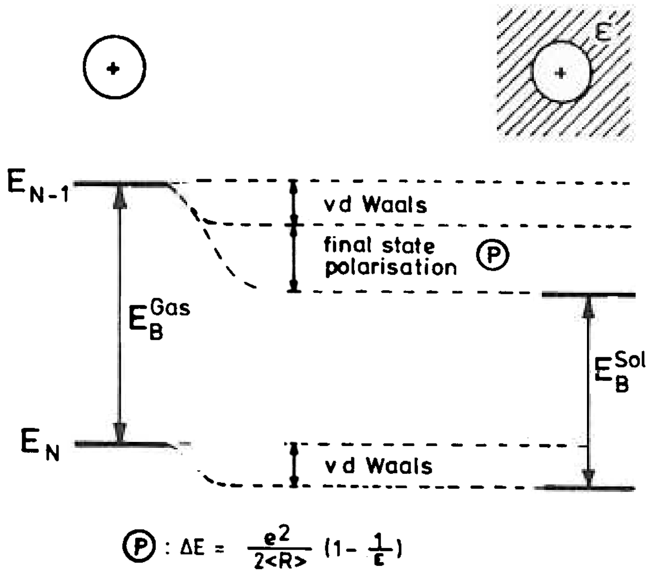


Fig. 2. Energy scheme for ionization of non-polar molecular solids. The polarization energy is taken from Refs. [13, 44].

3. Polar molecular solids

Considering the results of the previous section it was generally assumed that there is a one-to-one correspondence between gas and solid-phase photoelectron spectra. As a consequence, the interpretation of the solid phase spectra in particular of the core region, was mainly based on calculations done on the isolated molecular moiety. It is therefore not surprising that the core–hole spectra of polar donor–acceptor substituted aromatic molecules (D^+–Ar–A^-), e.g., para-nitroaniline and similar molecules, in the solid state have been interpreted following the above assumptions [26–36]. These species are a source of continuing interest from both experimental and theoretical viewpoints. This appears the case particularly for the simple nitroanilines where recent studies have addressed the nature of the usually large nonlinear second-order optical susceptibilities exhibited by these systems [4–7]. Of particular interest to us in this context is the unusual shape of heteroatom core-level ionization spectra reported for a series of D^+–Ar–A^- structures in the solid state [16–38]. The N1*s* (NO_2) level of PNA, for example, was shown to exhibit a characteristic doublet structure of approximately equal intensity ($\Delta E \sim 1.8$ eV) well separated from the apparently single component N1*s* (NH_2) emission occurring at lower binding energy as shown in Fig. 4 [21]. On the O1*s* peak, in addition, a relatively intense satellite to the high binding energy side (Fig. 4) is found [26, 27]. Pignataro and Distefano [26] have discounted extrinsic mechanisms, i.e., radiation damage as originally tentatively proposed by Siegbahn *et al.* [25], and showed these characteristic satellites to be inherent electronic processes, i.e., shake up transitions accompanying electron ejection. More recently Banna [16] reported gas phase XPS measurements on PNA. It was found [16] that the O1*s* spectrum was in good agreement with the solid phase results, whereas the nitrogen spectrum exhibited only the single components expected for the N1*s* (NO_2) and N1*s* (NH_2) primary core holes. Very recently, Ågren *et al.* [21] published the so far best resolved XPS spectra of PNA (Fig. 4) and showed that the apparently single gas phase N1*s* (NO_2) peak really consists of two components, i.e., an intense line at lower binding energy and a less intense satellite (ΔE = 1.25 eV) at higher binding energy. The ionization of these molecules represented one of the first examples to show a difference (more than a rigid shift) between molecular ionization in the gas and solid phase. Even without further explanation, it is clear that we cannot expect to find an appropriate description of such spectra of the molecular solid without consideration of solid state effects. In other words, calculations on the isolated molecule are not appropriate here. Almost at the same time as the experimental observation of the difference between vapour and condensed phase core spectra was published the authors had finished a first theoretical study [17] to investigate the influence of neighbouring molecules on the core ionization process in molecular solids. Using dimer models [17] we were able to explain the observations (summarized on the right hand side of Fig. 4). The bottom line of these studies was: The particular relative arrangement of the molecules in the solid enhances certain intramolecular screening processes and thus leads through intermolecular screening, not present in the isolated molecule, to the observed changes in the spectra upon formation of the solid. In other words, it is the dynamics of the core hole creation process that changes in the solid, and it is this aspect we want to concentrate on in the following.

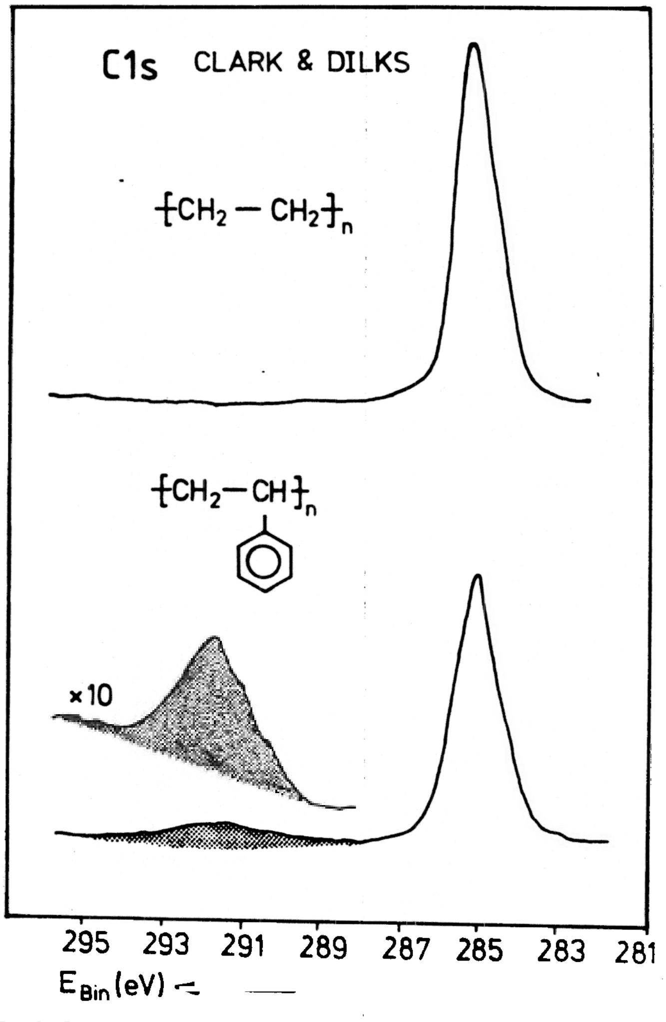


Fig. 3. C1*s*–ESCA-spectra of polyethylene (top) and polystyrene (bottom). The region of shake up structure has been shaded [49].

In order to understand the physics of the underlying processes we first have to consider the intramolecular processes in these dipolar donor/acceptor substituted aromatic systems.

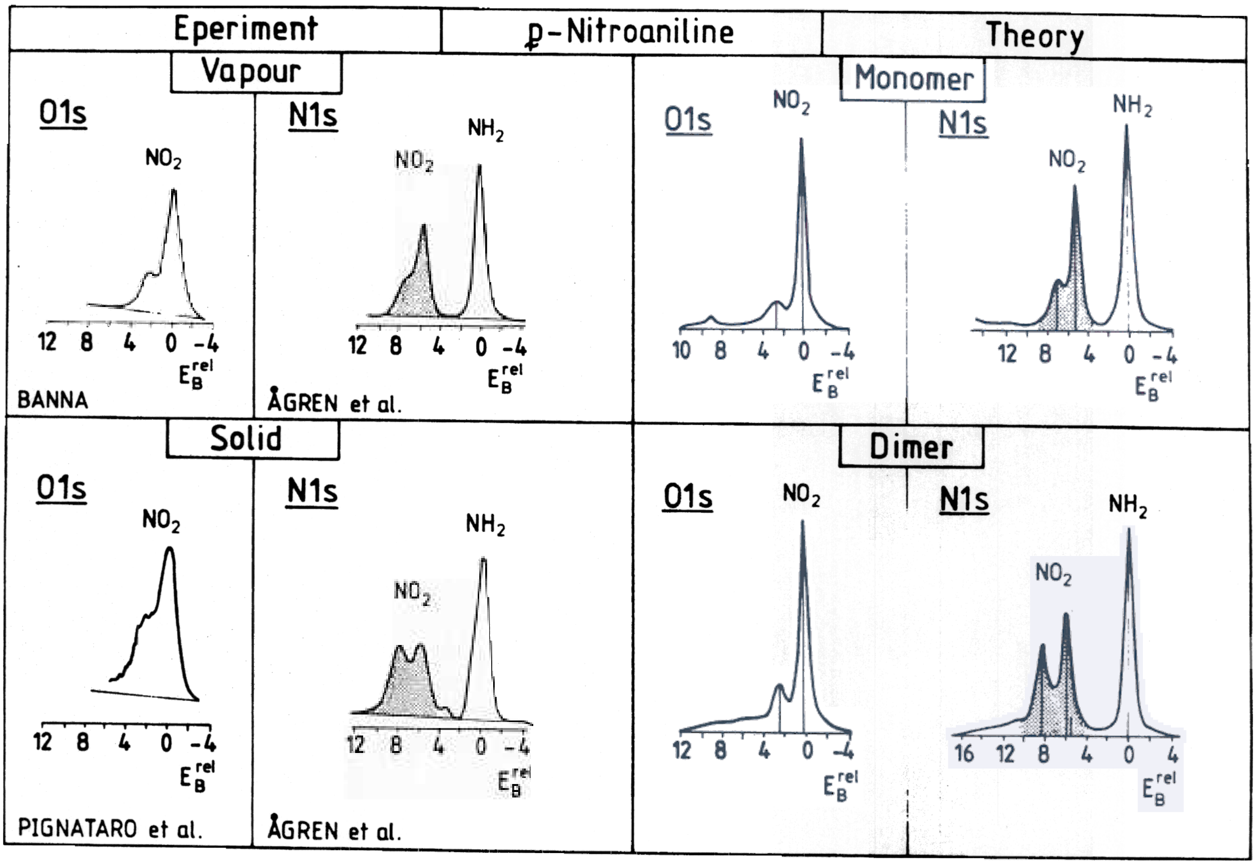


Fig. 4. N1*s* and O1*s*–ESCA spectra of para-nitroaniline in the gas phase [16, 21] and in the solid phase [21, 28] in comparison with calculated spectral functions for the isolated molecule and a dimer model to simulate interactions in the solid [18].

3.1. *Gas phase ionization*

Figure 5 shows the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the self-consistently calculated neutral, N1*s* (NO_2), N1*s* (NH_2) and O1*s* (NO_2) ionized PNA molecule [17]. In the neutral molecule the HOMO is localized on the six-membered ring and the NH_2 substituent, while the LUMO is localized on the ring system and the NO_2 group. This expresses the donor/acceptor nature of the compound, i.e., the NH_2 group being the donor, the NO_2 group being the acceptor. Upon core hole creation the electron distribution changes depending on the position of the core hole. If a N1*s* core hole is created on the NH_2 group those levels with large NH_2 character are pulled down in energy relative to those levels localized on the six-membered ring or on the NO_2 group [17]. Therefore, in the N1*s* (NH_2) ion the HOMO is no longer similar to the HOMO of the neutral, while the LUMO has basically the same shape as in the neutral. At the same time, the HOMO–LUMO energy gap increases. The charge distribution in the ion is, of course different from the neutral. In Fig. 6 the electron density difference between the

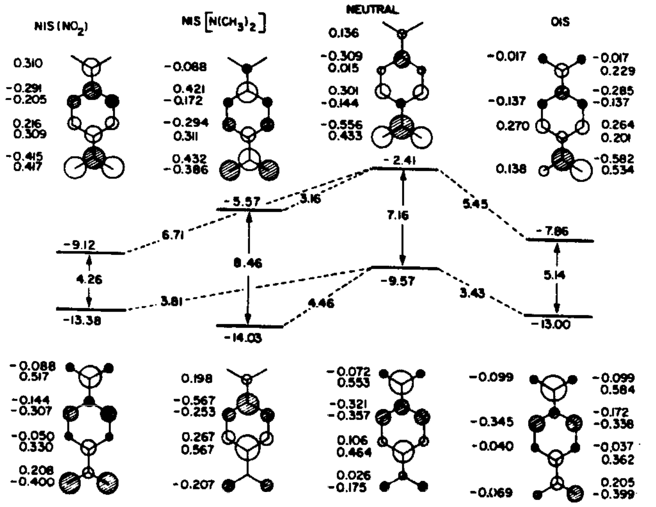


Fig. 5. Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of neutral, N1*s* (NO_2), N1*s* (NH_2 and O1*s* (NO_2) core ionized molecules. The circles correspond to the size of the p_π lobes of the constituing atoms. The phase is indicated by shaded and open circles [17].

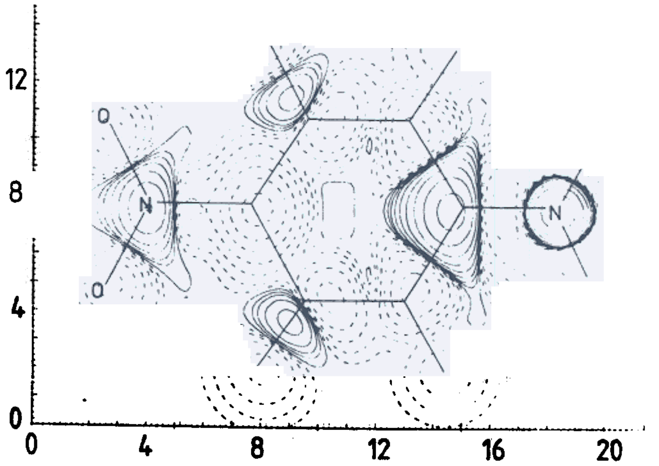


Fig. 6. Electron density difference plots ($\varrho_{PNA}^{N-1}(NH_2, N1s) - \varrho_{PNA}^{N}$) for the valence electrons only upon N1*s* core ionization of the amino group of PNA. Electron gain is indicated by full lines, electron loss by broken lines. The plotting plane is 0.5 Å above the molecular plane because the latter is a nodal plane for the π-electrons.

neutral and N1s (NH_2) ionized PNA is plotted. The plotting plane lies 0.5 Å above the molecular plane which is a nodal plane for π electron. Electrons are taken from everywhere in the molecule to screen the hole. This process is very effective, and screens the hole by 92%. Given these conditions, it is unfavourable to excite shake up transitions. Any excitation into the LUMO would help to transfer electrons towards the NO_2 group, i.e., away from the NH_2 group. This, in turn, would lead to a reduced screening, and thus to a reduced stability of the ion.

The situation changes qualitatively, if we create the core hole on the NO_2 moiety. The HOMO–LUMO gaps decreases, because the orbitals with NO_2 character are now stabilized. Consequently, the LUMO is pulled down in energy and gets, so to speak, partly occupied. In other words, the new occupied orbitals of the N1s (NO_2) ion have a strong admixture of LUMO (neutral) character, i.e., some more NO_2 character. This is shwon in Fig. 5. Analysis of the charge distribution in the core ionized state reveals that the state is screened, to about the same degree as the N1s (NH_2) ion state, i.e., 93%. However, in the case of the N1s (NO_2) state, excitation of electrons transfer electrons towards the hole and is thus a favourable process in the case of N1s (NO_2) ionization. Reasoning in this spirit was first introduced by Domcke *et al.* [33] on the basis of many body ab-initio calculations on PNA core ionizations.

Domcke *et al.* [33] proposed the term "negative shake up" to explain the PNA core hole spectrum. Briefly, they calculated the 2hp-shake up state involving the HOMO–LUMO excitation at lower binding energy than the normal hole state [33]. Usually, shake up excitations are assumed to have higher binding energies than the normal hole states. To a certain extend this nomenclature is misleading and connected with the calculation scheme used by Domcke *et al.* [33]. The method employed by Domcke *et al.* [33] refers to the molecular orbitals of the neutral system and describes the ion states as configuration superpositions within the basis of the neutral system. If one uses a different approach, where one primarily calculates the 1s hole state either directly [21, 36] or via the equivalent core approximation [17, 18] self-consistently, and then expands the core-excited (2hp) states within the basis of orbitals of the core ionized species, the introduction of the term "negative" shake up appears inappropriate. The state of lowest binding energy is the screened normal hole state and the shake up states are calculated at higher binding energy, i.e., they exhibit normal behaviour. Contact between the two schemes can be made by expanding the screened hole state orbitals within the basis orbitals of the neutral system [17]. The result is that the screened normal core hole state can be looked at as an unscreened core hole coupled to a HOMO–LUMO transition in the neutral. This transition transfers electrons from the NH_2 end of the system towards the NO_2 end and screens the hole. In other words, there is no fundamental difference between the two descriptions, there is only a semantic difference.

Still, even if the calculations are done on the core ionized system there is a debate about how to describe in detail the shake up transitions. Ford and Hillier [35, 36] performed ab-initio configuration interaction computations on the N1s (NO_2) and O1s (NO_2) ionized PNA using a FO–CI scheme and an explicit RHF hole state basis set (ΔSCF–CI). Both methods included selected doubly excited determinants in the CI expansion. Ford and Hillier [35, 36] found that the dominant contribution to the PNA core satellites of interest was the singly excited HOMO–LUMO configuration. Ågren *et al.* [21] also performed *ab-initio* computations on the N1s (NO_2) spectrum of PNA using a multiconfigurational self-consistent field (MCSCF) method and attribute the satellite structure especially to the doubly excited HOMO–LUMO transition. Ågren *et al.* [21] emphasized that the HOMO–LUMO singly excited configuration, favoured by Ford and Hillier [35, 36], provides only minor contributions to low lying satellite structure of interest. Ågren *et al.* [21] obtained excitation energies in good agreement with experiment, the intensity calculated for the satellite of interest is somewhat larger than found experimentally. Unfortunately, neither O1s (NO_2) spectrum, nor the N1s (NH_2) spectrum was calculated by these authors. Figure 7 shows the results of semiempirical CNDO/S–CI equivalent core computations including up to doubly excited configurations [18]. Since these calculations

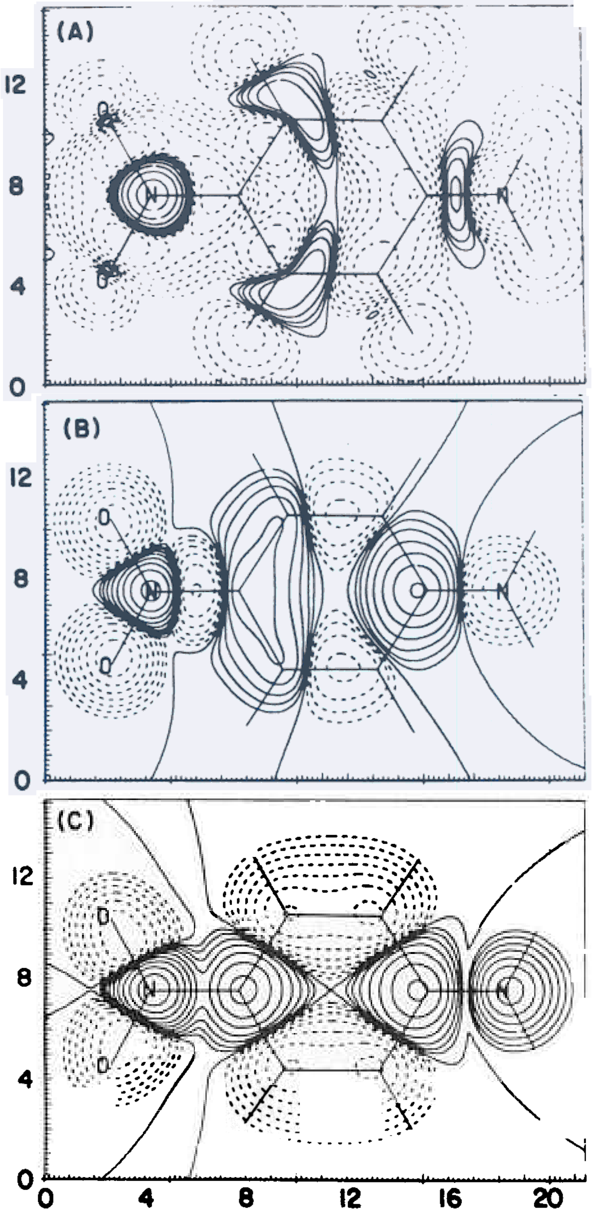


Fig. 7. Electron density difference plots for N1s-core-ionization of the NO_2 group of PNA. The plotting parameters are the same as in Fig. 6 [17]. (a) ($\varrho^{N-1\,\mathrm{GS}}_{\mathrm{PNA,N1sNO_2}} - \varrho^{N}_{\mathrm{PNA}}$) ground state (GS) core-ionized ion. (b) ($\varrho^{N-1,\mathrm{SU}}_{\mathrm{PNA,N1s,NO_2}} - \varrho^{N-1,\mathrm{GS}}_{\mathrm{PNA,N1s,NO_2}}$) lowest energy shake up (SU) state. (c) ($\varrho^{N-1,\mathrm{SU}\,N-1,\mathrm{GS}}_{\mathrm{PNA,N1s,NO_2}} - \varrho_{\mathrm{PNA,N1s,NO_2}}$) higher energy shake up (SU) state.

can be performed with less effort as compared to the above mentioned *ab-initio* calculations we have done all hetero-atom core ionization spectra (see Fig. 4). We concentrate in this section on the isolated molecule spectra (upper right hand side of Fig. 4). As observed experimentally [21] (Fig. 4) the N1*s* (NO_2) ionization yields only a relatively weak asymmetric feature on the high binding energy side of the primary peak ($\Delta E_{\text{theor.}} = 1.73\,\text{eV}$; $\Delta E_{\text{exp}} = 1.25\,\text{eV}$). The O1*s* ($NO_2$) spectrum indicates a shake up feature at ~2.8 eV [16]. The N1*s* (NH_2) spectrum is composed of a single peak, with no intense low lying shake up structure [21]. Our calculations [18] indicate, that the low lying shake up wavefunction for the N1*s* (NO_2) spectrum is composed of a mixture of the HOMO–LUMO singly excitation (60%) *and* the HOMO–LUMO double excitation (22%). Fig. 7b shows electron density difference plots for intense N1*s* (NO_2) shake up states. The plots represent differences between the excited (2h*p*) and the ground ion states. The low lying excited state [Fig. 7(b)] exhibits more intramolecular screening at the ionized nitrogen atom than calculated for the ionic ground state. Excited state screening occurs primarily through electron transfer from the NH_2 donor groups, and from the adjacent oxygen atoms. For the O1*s* (NO_2) spectrum we also find a dominating contribution by the single excited HOMO–LUMO transition.

Summarizing at this point we conclude, that even though the calculations reported up to date do not quantitatively reproduce excitation energies *and* intensities of the PNA shake up spectra, the qualitative analysis, presented above, includes the correct underlying physical ingredients involved in the dynamics of core hole screening process and shake up excitation in polar organic molecules.

While PNA is the prototype molecule for these studies, there have been reports on gas phase spectra of other systems belonging to the same class of molecules, i.e., 2-amino-6-nitronaphthalene [18], 1-amino-4-nitronaphthalene [18], p-amino-benzonitrile [37, 38], N,N-Dimethyl-p-nitrosoaniline [20], to name a few. All compounds exhibit more or less intense shake up structure, the details of which, of course, depend on the particular electronic structure. The most complex spectra, so far, have been reported for N,N-Dimethyl-p-nitrosoaniline [20]. They are shown together with calculated spectra in Fig. 8. The complete N1*s* ionization regions is particularly interesting since it consists of a relatively sharp "main" line and a shoulder that could, without further studies, be assigned as a shake up excitation associated with the most intense peak. However, a detailed theoretical analysis [20] shows (see calculated spectra) that the N1*s* (NO) core ionization is a multicomponent spectrum overlapping the essentially single line N1*s* [$N(CH_3)_2$] ionization. The fact that the observed chemical shift between the two N1*s* ionizations is so small turns out to be due to a rather complex compensation of initial and final state effects [20].

It should be mentioned at this point, that the dipolarity, i.e., the presence of donor and acceptor substituents is by no means a neccessary condition for a molecule to exhibit strong dynamic shake up effects. As shown by Slaughter *et al.* [24],

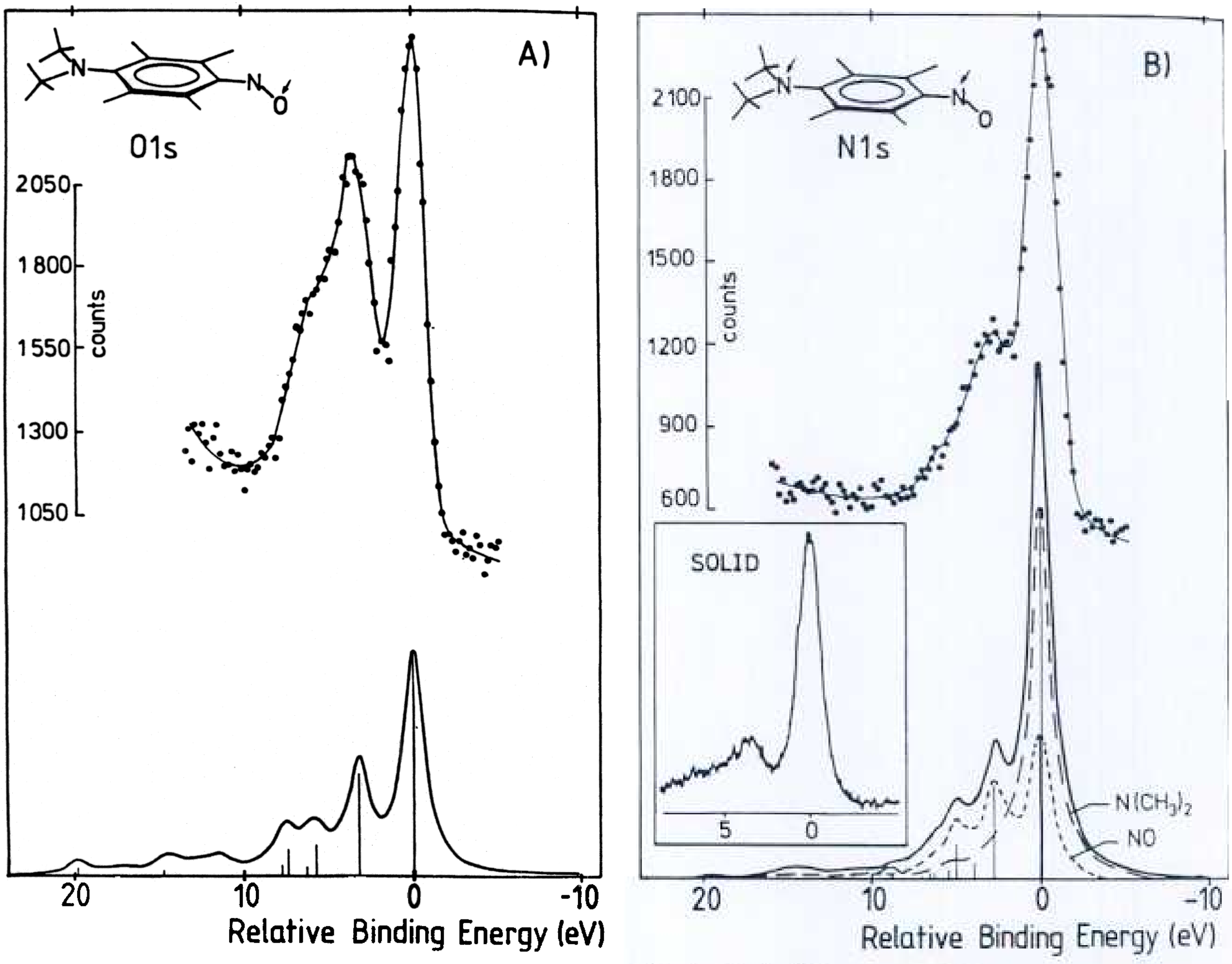


Fig. 8. N1*s* and O1*s*–ESCA spectra of N,N-dimethyl-para-nitrosoaniline [20] in the gas phase in comparison with calculated spectral functions for the isolated molecule. The insert as the N1*s*-spectrum shows the experimental spectrum taken of a solid sample [72].

nitrosobenzene is a clear example of a system with a single substituent that shows intense shake up transitions in the gas phase. A detailed computer simulation [19] of the spectra revealed that a similar charge-transfer screening process takes place as in the dipolar compounds. The main charge-transfer in nitrosobenzene is connected, however, with the ring π-electrons of the six membered ring, and with the oxygen atom. Nitrosobenzene is one of the few cases, where in addition to the core ionization spectra of the substituents, the C1*s* core ionization spectrum has been reported [24]. Interestingly, Slaughter *et al.* [24] find weak shake up structure corresponding in energy and intensity to the C1*s* shake up structure in benzene [41]. Once more, this fact reflects the rather high degree of localization of the core hole. Also, as far as the shake up excitations are concerned, only those excited states with a high wavefunction amplitude at the core ionized site are probed (see Appendix).

So far we have concentrated on core ionizations in these polar molecules. The appearance of shake up transitions is, however, not limited to the core region. In recent years experimental and theoretical results have been published indicating the existence of shake up satellites also in the valence region [50–62]. In particular, Bigelow [51, 61] has emphasized this fact for the case of PNA above 10 eV binding energy. Figure 9 shows a comparison of experiment [63] with calculated intensity distributions [51], of which the middle panel includes shake up excitations [51]. The dashed lines between the intensity distributed calculated via Koopman's theorem and the SCF-ion-state calculation show how the hole state configuration correlates with various excited ion state configurations (not specified here) [51]. For example, the splitting of the third Koopman's state near 11 eV binding energy into two components of almost equal weight around 10 eV and 13.4 eV is caused by the HOMO–LUMO intramolecular charge-transfer excitation with the hole state localized on the oxygen atoms. The situation is therefore quite analogous to the core ionization.

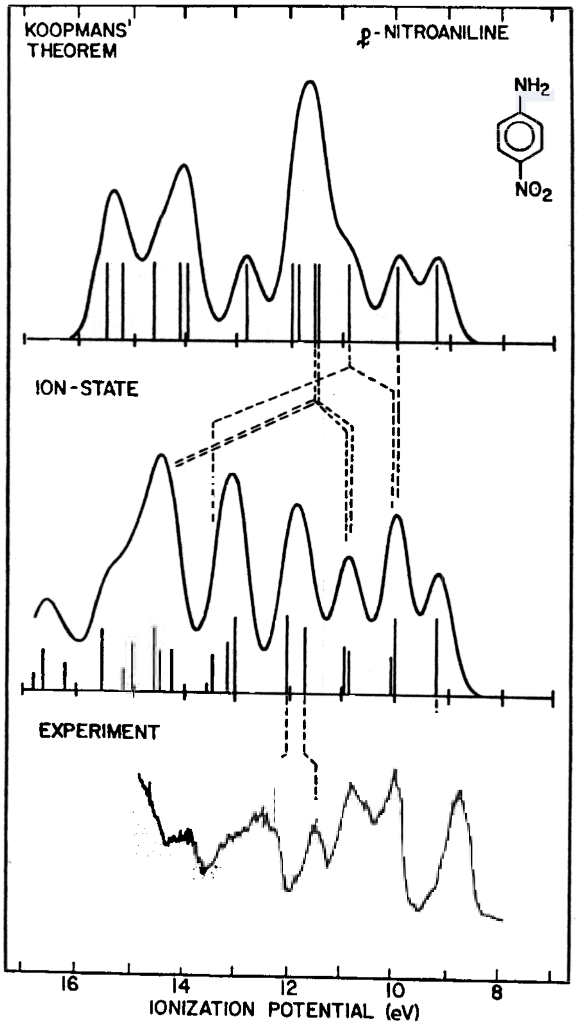


Fig. 9. Comparison of calculated valence ionization spectra of PNA after Bigelow [51]. (a) According to Koopman's theorem. (b) After self consistent calculation of the ionic ground state, and CI for the calculation of higher excited hole and 2h*p*-states. (c) Experimental HeI spectrum [63].

3.2. *Solid phase ionization*

In the following we want to address the modifications observed for dipolar molecules (see Fig. 4) upon going from the gas phase to the solid phase. Obviously, as revealed by Fig. 4 for PNA the influence of the solid environment on the core-hole spectra (on which we want to concentrate in the first part of this section) is not uniform in the sense discussed for benzene. Rather, we find specific alterations of the shake up structure of certain core ionizations, while other core ionizations do not appear to be modified at all, except for the above discussed polarization shifts. To discuss the mechanisms behind these observations we first have to consider the crystal structure of these polar molecular solids. Figure 10(a) shows as an example the arrangement of PNA molecules in the solid. (At room temperature PNA forms a solid.) Trueblood, Goldish and Donahue [64] showed that the molecular packing exhibits intermolecular nitro-amino contacts ("long" hydrogen bond-

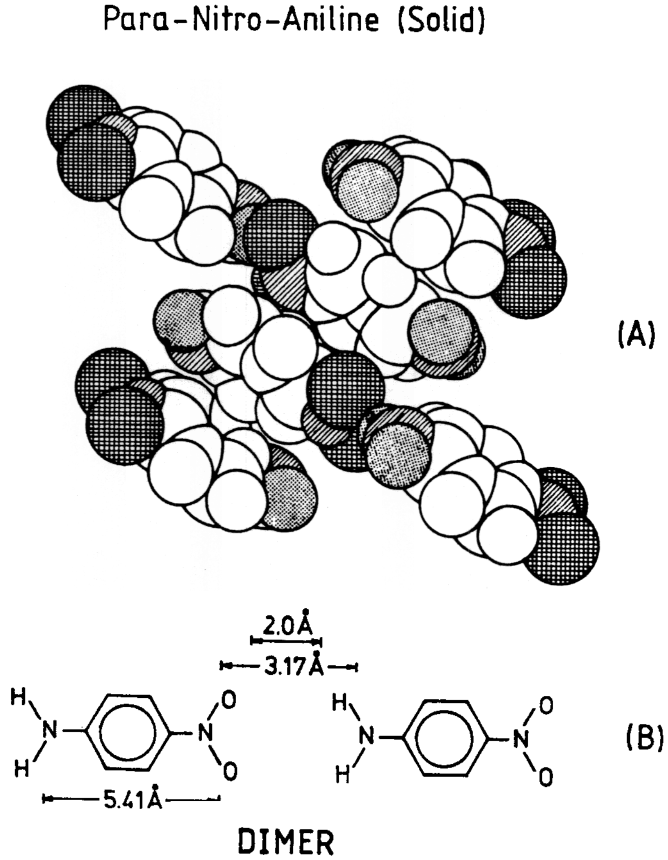
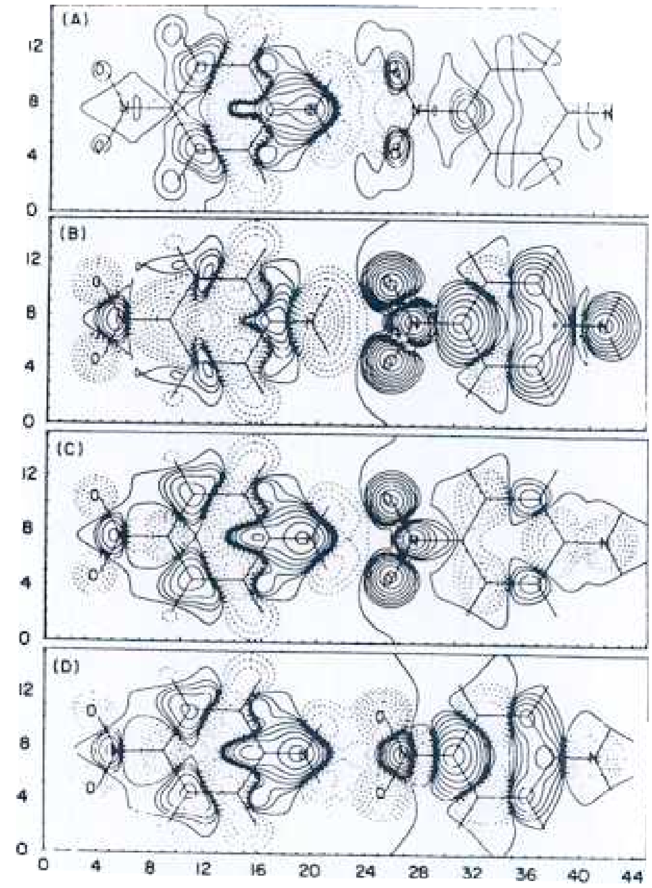


Fig. 10. Intermolecular arrangement of PNA molecules in the solid as taken from Ref. [64] (top). Dimer model system [17] used to describe intermolecular interaction in the solid.



charge flux between the molecules, however, is relatively small (~ 0.05 e per moiety). This is reflected in the magnitude of the dimer dipole moment which increases by only 3% relative to the sum of the dipole moments of the separated molecules [18]. In other words the change of the electronic structure in the neutral ground state is rather limited. In the following we shall find the changes in the final ion state due to intermolecular interactions to be considerably more pronounced. Fig. 11(b–d) show electron density difference plots for the relevant ion states of the dimer upon N1*s* (NO_2) ionization. The superimposed electron density obtained from a non interacting neutral PNA and a N1*s* (NO_2) core ionized PNA-moiety has been substracted from the coupled dimer state. Figure 11(b) displays the corresponding plot for the core-ionized dimer ground state. This state exhibits strong intermolecular charge-transfer, which occurs in addition to the intramolecular charge-transfer towards the core ionized nitrogen atom. In this state which only exhibits rather low spectral weight (Fig. 4) the intermolecular screening charge is delocalized over the complete ionized PNA moiety. There is another intermoleculary screened state of the dimer system which shows up with the largest intensity. This state, shown in Fig. 11(c), localizes the *inter*molecular screening charge on the NO_2 moiety, preferentially on the oxygen atoms, which provided considerable *intra*molecular screening charge in the core ionized ground state of the isolated molecule. It is therefore reasonable to relate the most intense line of the core

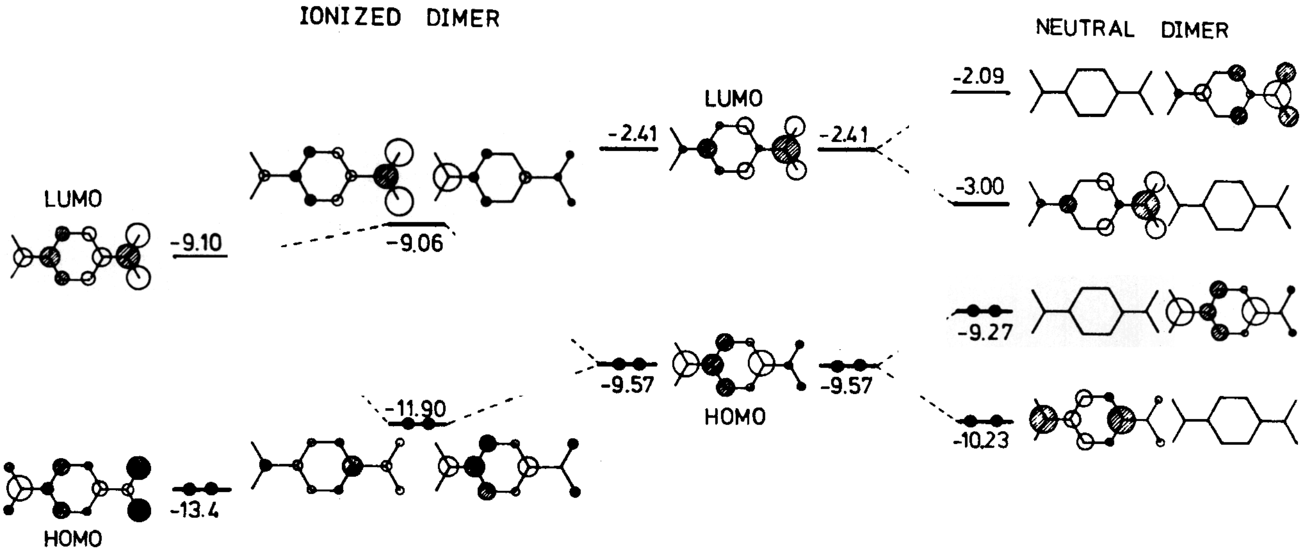


Fig. 12. Wavefunctions and energies of HOMOS and LUMOS of the neutral dimer (right-hand side), the neutral monomer, the N1*s* (NO_2) core ionized dimer (left-hand side), and the corresponding core ionized monomer. The diagram has been constructed based on Refs. [17, 18].

ionized dimer to the main line of the isolated molecule, modified through *intermolecular screening*. The intermolecular screening stabilizes the core ionized ground state relative to the isolated system. The intense shake up state ~2.6 eV above the ground ion state, represented by Fig. 11(d), shows the characteristics of the corresponding shake up 1.7 eV above the ground state of the isolated ion. If appears that this shake up which is more effectively screened intramolecularly, is only slightly affected by intermolecular screening.

Summarizing, we find on the basis of a dimer model, a very reasonable qualitative explanation for the change in the spectral function upon condensation: The ground core ionized state of PNA, which in the isolated molecule is intramolecularly screened gains stabilization energy by intermolecular charge-transfer screening from neighbouring molecules, while the shake up state known from the gas phase experiences much less intermolecular screening. This increases the energetic splitting of the two lines in the spectrum as observed experimentally. Concomittantly, the core ionized N1*s* (NO_2) ground state changes its character, i.e., its wavefunction with respect to the isolated molecule. In contrast the wavefunction of the molecule in the neutral ground state of the solid is still very similar to that of the free molecule. Therefore, the projection amplitude that governs the intensity of ionization decreases upon formation of the solid.

The above analysis is based on calculated charge density distributions. It is also possible and, for further insight, helpful to investigate how a one-electron picture can rationalize the observations and computational results. For this purpose we show in Fig. 12 an orbital scheme based on orbitals of neutral and core ionized PNA. It shows on the right hand side the neutral dimer and on the left hand side the N1*s* (NO_2) ionized dimer. In the neutral, the electrostatic interaction between the two PNA moieties lifts the degeneracy of HOMOS and LUMOS without strong orbital mixing among the moieties. There is obviously no large overlap between the HOMOS and LUMOS of the neutral because they are localized on opposite ends of the molecules. Consequently, we expect a rather weak distortion of the electron distribution in the dimer in line with our discussion above. The situation changes upon core ionization. The core ionization leads to a stabilization of levels of the ionized moiety on a common energy scale with respect to the levels of the neutral as indicated, and the shape of the orbitals changes as discussed above. The HOMO and LUMO of the ion, which both have NO_2 character can now interact with the orbitals of the neutral due to the larger overlap. The orbitals on different moieties mix which is equivalent to saying that charge is exchanged between the moieties. Clearly, there are two parameters that determine the intermolecular interaction mechanism. (i) the energetic separation of the relevant ionic levels from those of the neutral; (ii) the intermolecular overlap between the ion orbitals and those of the neutral. Figure 5 indicates how these parameters change for the various core holes. The LUMO of N1*s* (NO_2) ionized PNA is close to the HOMO of neutral ($\Delta E = 0.45\,\mathrm{eV}$), for the O1*s* ($NO_2$) the separation is still 1.71 eV, which leads us to expect a smaller change of the spectral function upon condensation for O1*s* (NO_2) ionization in comparison to N1*s* (NO_2) ionization. For the N1*s* (NH_2) ionization the LUMO(ion)–HOMO(neutral) separation is $\Delta E = 4.0\,\mathrm{eV}$. In this case we therefore expect the smallest effects. This is in full agreement with experimental observations (Fig. 4). The above reasoning provides us with a set of simple criteria to rationalize the observed variaton in the spectral functions on going from the vapour phase to the solid phase spectra. It also allows us to predict whether such variations are to be expected. To this end it is important to stress again that the observed effects are induced by the creation of the core hole and are thus final ion state effects as opposed to initial state effects. However, the relative orientation of the molecules in the crystal, i.e., the NO_2–NH_2 contacts, are a necessary condition in the case of PNA. In fact, it has been proposed that formation of hydrogen bonds by this arrangement in the solid may perturb the gas phase orbitals in such a manner that *intramolecular* coupling of the core hole and the valence excitations is enhanced and the spectral function is modified [21]. Owens and coworkers [39] recently noted, and subsequently rejected, the notion that the condensed-phase multipeak core-hole spectra of poly (nitroaromatics) were due to asymmetries in the molecular environment. However, there is further evidence, that the above mentioned final state effects represent the leading mechanism

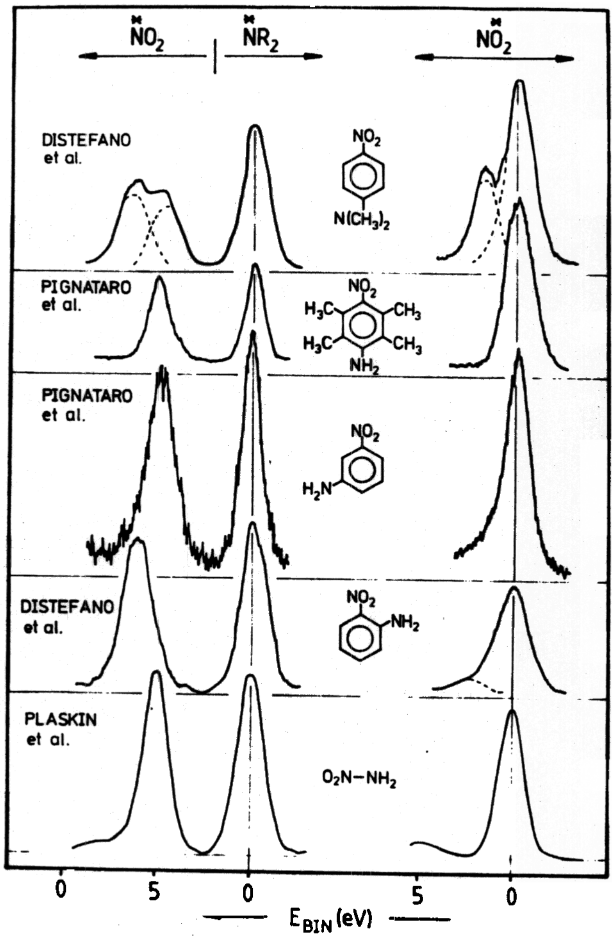


Fig. 13. N1*s* and O1*s*–ESCA spectra of a collection of dipolar aromatic molecules [26, 28] in comparison with N,N-dimethyl-nitramine [68].

to cause the observed changes: It is generally accepted that hydrogen bonding can be prevented by replacing the hydrogen atoms in question by methyl groups. In this spirit one expects that N,Ndimethyl-PNA should not exhibit the changes in the spectral function upon condensations if hydrogen bonding is the cause of the effect. However, the spectra (solid see Fig. 13) are almost identical to the unsubstituted PNA, thus corroborating the above discussion of final state effects.

A similar analysis for the region of valence ionizations remains to be done. We could expect corresponding effects in this region, since we have seen in the previous section that shake up is probable in the valence region. To our knowledge this aim has not been achieved yet but it appears to be an interesting project, although we expect the analysis to be more difficult than in the core region.

At this point it should be quite clear, that there are distinct variations between gas and solid phase spectra, and that it may be dangerous to interpret spectra taken on solid samples of polar organic molecules in terms of rationalization schemes based on the isolated molecule.

Nevertheless, it is quite instructive to compare dipolar organic molecular solids where the structural parameters of the molecules differ. Fig. 13 shows selected solid phase data collected from the pioneering work of Pignataro and Distefano [26–28] and others [68]. At the top N,N-dimethyl-p-nitroaniline with its characteristic spectral function is presented. If the ring hydrogen atoms are substituted by methyl groups, the NH_2 groups as well as the NO_2 groups cannot assume a coplanar arrangement in the moiety. In addition the separations in the solid differ from PNA in such a way that the intermolecular coupling is substantially weakened. The same is true for the metasubstituted 3-nitroaniline, and the 2-ortho-nitroanilines. The solid state structure is greatly different from paranitroaniline and there is no obvious possibility for strong intermolecular coupling. Therefore, all these spectra show the expected behaviour, i.e., weak or negligible shake up intensity.

For comparison with the disubstituted aromatic molecules we show the N1*s* region of N,N-dimethylnitramine [68]. Without detailed consideration it may be somewhat surprising that if the amino group is directly coupled to the nitrogroup there is no shake up structure observed. The reason for this observation is rather obvious. Since the two subsystems are *strongly coupled via the N–N* covalent bond, the orbitals are delocalized over the complete system. Because strong shake up excitation depends on localization of subsystem orbitals and coplanarity, it is obvious why such effects are not observed for this system. We can therefore think of the benzene ring in PNA to act as a spacer between the donor and the acceptor groups which, at the same time keeps the two groups co-planar. There is yet another class of organic molecular solids which is formed by condensation of polar organic molecules. Nitrosobenzene [24] is an example. These molecular solids are characterized by actual *weak covalent bond formation* between the monomer moieties. In solid nitrosobenzene Dieterich *et al.* [69] have proven the existence of nitrosobenzene-dimer moieties via X-ray scattering. The local geometric arrangement of substituent and aromatic ring is very different from the gas phase. While the nitrosobenzene molecule is basically planar, the two NO-substituents *cis*-dimerize forming a weak N–N bond with the two NO-substituents forming a planar system, and the aromatic ring planes twisted to be perpendicular to the $(NO)_2$-plane. This destroys the π-coupling between the ring and the substituent and one would expect that this has a major influence on the N1*s* spectral function. Indeed, the excitation energies, as well as the relative shake up intensities change but the variations are rather small as shown in Fig. 14. The solution to this problem is found by considering screening within the $(NO)_2$ moiety. It is known from core ionization spectra of condensed NO, where NO-dimers are formed, that the N1*s* spectrum of the solid shows intense shake up due to intermolecular screening between the two NO moieties of the dimer [70–71]. Detailed calculations for the nitrosobenzene dimer shows [19], that in this case a similar mechanism is active. Instead of screening the N1*s* hole by transfering electrons from the benzene ring, which is the important process in the free molecule, it is intra$(NO)_2$-group-screening in the solid. Referring to the isolated nitrosobenzene molecule we can call this process again intermolecular screening. The situation, however, is slightly different, since the two molecules interact in the neutral via a covalent bonding interaction. Again, the shake up is a clear final state effect.

From this study, some interesting questions for future experimental and theoretical studies arise. For example: What happens if we force the benzene rings to π-couple to the $(NO)_2$ moiety, or how different is the spectral function for a *trans*-$(NO)_2$ moiety? One can taylor molecules to directly address such questions. Investigations on [72]

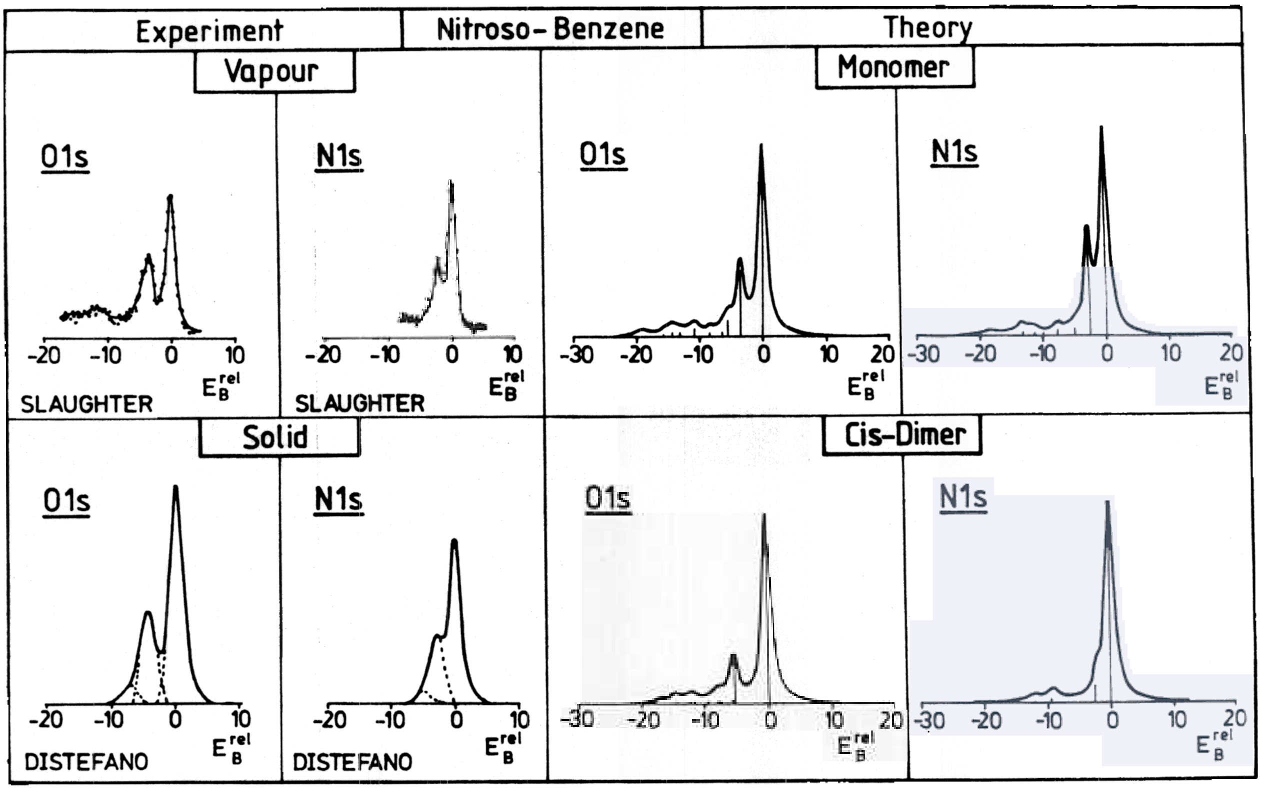
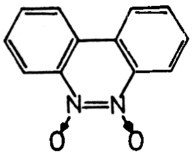
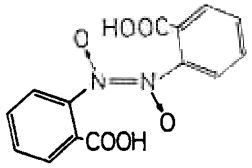


Fig. 14. N1*s* and O1*s*–ESCA spectra of nitrosobenzene in the gas phase [24] and in the solid phase [28b] with calculated spectra based on the isolated molecule [19] and on a *cis*-nitrosobenzene-dimer (geometry from Ref. [69]).



for instance are under progress to tackle the first questions posed. In connection with the second question the molecule



is of considerable interest [69].

Finally, it should be mentioned that differences between gas and solid phase photoelectron spectra have been observed for other systems. Particularly interesting cases, of considerable importance, are the amino-acids that form Zwitter-ions upon condensation. Salaneck and collaborators [73] have recently started to study these systems. Of course, there are other ionic or zwitter-ionic molecular solids which exhibit intense dynamic effects, e.g. pyridinium and pyrylium salts [74], and very recently these effects have been observed in squaraine derivatives [75]. In the former case [74], the observed spectral function has been shown to depend on the relative position of the two counter ions.

4. Conclusions

We have shown that for a certain class of dipolar organic molecular solids *strong dynamic shake up effects* are introduced *due to intermolecular interaction in the ionized molecular solid.* Para-nitro-aniline is the most prominent example for a compound showing these effects. Simple physical criteria are developed that allow us to predict the conditions under which one has to expect an influence of the solid: Upon (core)-ionization the levels of the ionized molecule are stabilized with respect to the levels of the surrounding matrix of neutral molecules because the hole remains localized on the ionized molecule. In fact, the LUMO of the ion can come energetically close to the HOMO of the neutrals. It is now crucial to have the appropriate relative orientation of the molecules within the molecule. If the neutral molecules carry electron releasing groups such that overlap between the ion LUMO and the neutral HOMO is probable charge can be exchanged between the subsystems, and intermolecular screening of the hole results. This is the leading mechanism that changes the spectral function on going from the gas phase to the solid phase. The same situation should be valid in the case of valence ionizations but has so far not been explored, except for only very few exceptions, i.e., see Refs. [22, 23, 76]. A special case of this type of ion state enhanced intermolecular interaction occurs in those organic molecular solids where molecules aggregate upon condensation and form weak covalent intermolecular bonds. Nitrosobenzene has been discussed as an example.

Finally, it should be pointed out that the dynamic phenomena observed in organic molecular solids are conceptually very similar to those found in connection with core-ionized of molecular adsorbates [77–80]. This connection has been pointed out by several groups and is only mentioned here [17, 21, 33].

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Appendix: Ionization probabilities

The spectral function depends on the conditions of how the final ion states are "prepared" by the incoming photon. In a half-classical sense we can use the following picture [A1]: By absorption of a photon an electron–hole pair, i.e., a dipole, is created. The electrons in the system collectively screen the dipole. As the electron created through the electron–hole pair diffuses away from the hole the remaining electrons in the system tend to assemble around the hole and to avoid the electron. In other words, the hole dependent effects can, in general, not be separated from the electron dependent effects. This is particularly important near the ionization threshold. An exact quantum mechanical calculation is extremely elaborate, and one usually considers two limiting cases, i.e., the adiabatic and the sudden limits. In the adiabatic limit one assumes that the electron is ejected so slowly that the system is always in its state of lowest energy. If, on the other hand, the electron is ejected instantaneously so that the remaining electrons cannot follow the sudden change in the potential, then the created hole state is not an eigenstate of the ion. However, this virtual state propagates into the eigenstates of the system and populate in general, a variety of excited states. If one of the states has a relatively high intensity we call the corresponding line in the spectrum the "main" line. Those lines with lower intensity are called shake-up and shake-off satellites, depending on whether the excited electron is bound or unbound [A2]. The following discussion tries to evaluate how one can numerically try to calculate the transition rates for such processes.

The transition probability between two eigenfunctions ψ_A and ψ_e of a common Hamiltonian is given by Ref. [A3]:

$$\sigma(\omega) = \frac{2\pi}{h}|\langle\Psi_e|H'|\Psi_A\rangle|^2\delta(E_e - E_A - h\omega) \tag{A1}$$

if the perturbation H' is small.

For an electromagnetic field H' can be chosen as [A4]

$$H' = \frac{e}{2mc}(A \cdot p + p \cdot A) + \frac{e^2}{2mc^2}A^2 \tag{A2}$$

For one-photon ionizations one can eliminate terms quadratic in A and rewrite the expression [A5] in terms of annihilation and creation operators (a_K, ${}^{+}a_1$):

$$\sigma(\varepsilon) = \frac{2\pi e^2}{m^2c^2h}|\sum_{k,l} M_{k,l}\langle\psi_e|a_k \cdot {}^{+}a_l|\psi_a\rangle|^2 \times \delta(\varepsilon - K_{kin})\delta(E_E - E_A - h\omega) \tag{A3}$$

with:

$$M_{k,l} = \langle\phi_K(n)|A_n \cdot p_n|\phi_l(n)\rangle \tag{A4}$$

for electron n in one-particle states ϕ_k, ϕ_l, and E_{kin} the kinetic energy of the ejected electron. In order to calculate this quantity we have to calculate the one-electron integrals $M_{k,l}$ as well as the electron-hole integrals. $M_{k,l}$ contains information about, e.g., the angular dependence of the ionizations, the electron-hole integrals contain the internal degrees of freedom of the system, e.g., vibrational structure and, spin-orbit couplings. Due to the difficulties to calculate $\sigma(\varepsilon)$ directly we introduce a hierarchy of approximations:

1. *The final state of the electron ejection process can be described by an antisymmetrized product of one-electron state of the ejected electron $\chi_e(n)$ and the remainings $(N - 1)$ electron system ($\psi_{e,E}^{N-1}$)* [A5]

This leads to the neglect of correlation of the ejected electron and the remaining ion. Then $\sigma(\varepsilon)$ is:

$$\sigma(\varepsilon) = \frac{\pi 2e^2}{m^2c^2h}|\sum_{k,l}\{M_{e,k}\langle\psi_{e,E}^{N-1}|a_k\psi_A\rangle + m_{e,k}\sum_{i,j} M_{i,j}\langle\psi_{e,E}^{N-1}|a_i \cdot {}^{+}a_j|a_k\psi_A\rangle\}|^2 \times \delta(\varepsilon - E_{kin})\delta(E_{e-A} - h\omega) \tag{A5}$$

with:

$$m_{e,k} = \langle\chi_e(n)|\phi_k(n)\rangle. \tag{A6}$$

The dipole operator connects the initial one-electron state ϕ_k directly with the active continuum state χ_e, in the first term of the k-sum, whereas in the second term it connects only the passive orbitals of the $(N - 1)$ electron system with the continuum state. We call the transitions dominated by the first term "direct" and those dominated by the second term "conjugate".

2. *The energy of the ejected electron is large* [A1, A7]

Under this condition it is generally assumed that the first term dominates and we get:

$$\sigma(\varepsilon) = \frac{2e^2\pi}{m^2c^2h}|\sum_{e,k} M_{l,k}\langle\psi_{e,E}^{N-1}|a_k\psi_A\rangle|^2 \times \delta(\varepsilon - E_{kin})\delta(E_e - E_A - h\omega) \tag{A7}$$

3. *The initial one-electron state is well separated in energy from other one-electron states*

This reduces the k-sum to a single term and avoids interference between various hole states:

$$\sigma(\varepsilon) = \frac{2e^2\pi}{m^2c^2h}|\sum_{e} M_{l,k}\langle\psi_{e,E}^{N-1}|a_k\psi_A\rangle|^2 \times \delta(\varepsilon - E_{kin})\delta(E_e - E_A - h\omega) \tag{A8}$$

and we arrive at the well known equation that is generally the starting point of a numerical analysis. To evaluate eq. (A8) ψ_A and $\psi_{e,E}^{N-1}$ have to be calculated. Usually, many particle states are calculated within a configuration interaction scheme.

$$\psi_{e(A)} = \sum_n c_{n,E(A)}|\psi_{E(A)}^n\rangle$$

where the $c_{n,E(A)}$ determine the extend to which various configurations $\phi_{E(A)}^n$ mix. These configurations are usually generated by creation of single, double, and other multiple excitations with respect to a reference configuration. Obviously photoionization peak intensities can be influenced by configuration interaction. We differentiate two extreme cases: (i) ground state correlation, (ii) final state correlation. In the case of the core hole spectra of donor–acceptor substituted aromatic molecules we use the equivalent core state as the reference configuration. For an equivalent core molecule with closed valence shells, i.e., $NC_5H_6^+$ vs. C_6H_6 [A8] a valence excitation leads to singlet and triplet excited states that have to be thought to be coupled with the (formally non existing) core spin to form doublet states [A9, A10]. Usually, the main contributors to the shake up spectrum are the singlet coupled doublet states, since in first order the intensity of the triplet coupled doublet vanishes. A way, for the triplet coupled to gain intensity is by coupling between the singlet and the triplet coupled doublet states [A11]. In the case of rather intense shake up structure, the latter process is not very important, and one can assume, that the singlet doublet states dominate the shake up spectrum. The p-nitro-aniline shake up spectrum is, therefore, governed by the latter excitations. However, for systems where the shake up spectrum is of rather low intensity, i.e., for benzene, triplet coupled doublet states may be important [A11].

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