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C 1s photoemission and shake-up features of $(C_{59}N)_2$

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Abstract. We report on a study of the C 1s shake-up spectrum for bulk films of $(C_{59}N)_2$ and find a previously unobserved peak at 1.05 eV from the main line. This new peak can be attributed to the C 1s binding energy of sp^2 -like carbon atoms bound directly to nitrogen. We further analyse the spectrum by comparing it to a convolution of valence band and x-ray absorption spectra, which closely mimics the transitions possible in the presence of a core hole. The shake-up spectrum represents on-site excitons, and their onset is consistent with the optical gap of 1.4 eV.

In the past 20 years members of the fullerene family have found their way into all areas of surface science, nanotechnology and device fabrication. This is hardly surprising, as the extremely versatile parent compound C_{60} can be easily altered to enhance the desired electronic properties and structure. It can be functionalized and doped in a number of ways, including exohedral doping by alkali metals, endohedral doping through inclusion of an atom or cluster, and through substitutional doping by replacing carbon atom(s) by different species, such as nitrogen or boron. The first heterofullerene synthesized in this way was $C_{59}N$, also known as azafullerene. In this molecule the replacement is effectively a form of n -type doping, and the substitution affects the bonding of the carbon cage such, that the preferred structure at room-temperature is a $(C_{59}N)_2$ dimer, where an intermolecular sp^3 -like bond between two carbons neighbouring the nitrogen atoms is formed. This gives the $C_{59}N$ unit essentially three different types of carbon environment. The majority (56 C atoms) resemble the sp^2 -like C_{60} carbons, a further two sp^2 -like atoms are bound to 2 carbon and 1 nitrogen atom, and there is 1 carbon atom bound to nitrogen and involved in the sp^3 -like dimer bond. Photoemission spectra of the carbon 1s peak, however, have to date not revealed these two additional carbon species as their spectral signature can be expected to overlap with the strong shake-up structures.

All experiments were performed at room temperature and at normal emission at the undulator beam line I311 at the MAX II storage ring in MAXlab, Lund, Sweden. The overall resolution was 30 meV for valence band photoemission (PES), 75 meV for C 1s PES, and around 80 meV for the C K-edge near-edge x-ray absorption fine structure (NEXAFS) spectrum, taken in Auger yield mode. All spectra were normalised to the ring current and the NEXAFS spectrum

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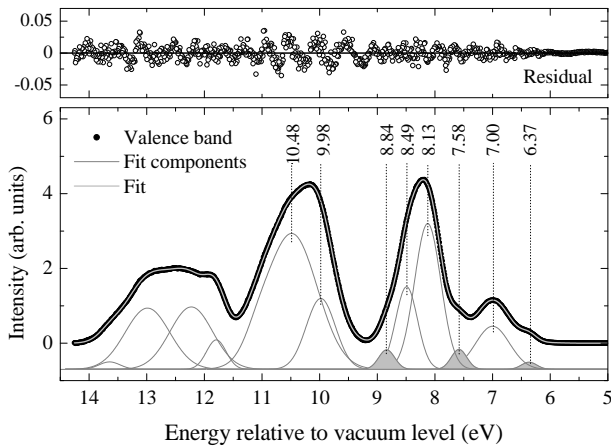


Figure 1. Gaussian peak fit to valence band spectrum, after subtraction of a Shirley-type background. Shaded peaks are related to the effects of N substitution and dimerization.

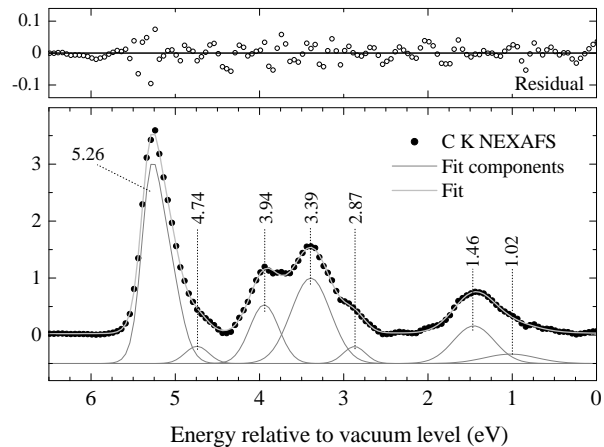


Figure 2. Gaussian fit to the C K NEXAFS spectrum, after subtraction of a Shirley-type background. The LUMO is fitted by an asymmetric Gaussian.

has been corrected for the photon energy profile of the beamline by measurements on a clean Ag:Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° substrate [1]. Energy calibration of the photon energy was achieved by measuring strong photoemission peaks in first and second order light. The binding energy of the photoemission and NEXAFS peaks was determined relative to the vacuum by means of bias voltages of 7 and 10V on the sample [2]. No signs of charging were observed. The azafullerene molecules used in this study were prepared and purified [3] and deposited at 400-450 °C to give a thick film (ratio N:C \sim 1:60) [4].

Fig. 1 shows the characteristic valence band (VB) spectrum of $(C_{59}N)_2$ referenced to the vacuum level, after subtraction of a Shirley-type background. Although similar to C_{60} , the influence of the nitrogen substitution is evident: first, the stronger core potential offered by the nitrogen atom manifests itself in a low binding energy shoulder split off from the highest unoccupied molecular orbital (HOMO), which carries significant nitrogen character [5]. This is, however, not to be associated with simple filling of the C_{60} lowest unoccupied molecular orbital (LUMO), as the excess electronic charge stays relatively localized on the nitrogen sites. Second, dimerization itself, and the consequential lowering of the molecule's symmetry, also contributes to the formation of this low binding energy shoulder and introduces further changes to the electronic structure, observed as broadening and two extra structures surrounding the C_{60} -like HOMO-1 valence band peak, which is not unlike the effects of C_{60} dimerization at low alkali doping levels [5, 6].

In Fig. 2, on the same energy scale, we have plotted the carbon K-edge NEXAFS spectrum, which is a measure of the carbon partial density of unoccupied states (P-DUS). The energy gap between the new $(C_{59}N)_2$ HOMO and the carbon LUMO is \sim 1.1 eV (peak to peak). Similar experiments have been performed to give the nitrogen P-DUS and have revealed that the overall LUMO of $(C_{59}N)_2$ has predominantly carbon character (see [4]).

In order to trace the origin of the different shake-up structures (see below), fits have been made to the VB and NEXAFS spectra. The decomposition into Gaussian peaks is plotted underneath the data in Fig. 1 and Fig. 2, and compares well with the theoretical density of states [5]. In order to introduce only the minimal amount of components needed, certain closely packed levels are represented by a single peak in our fits. The carbon LUMO is fitted by an asymmetric

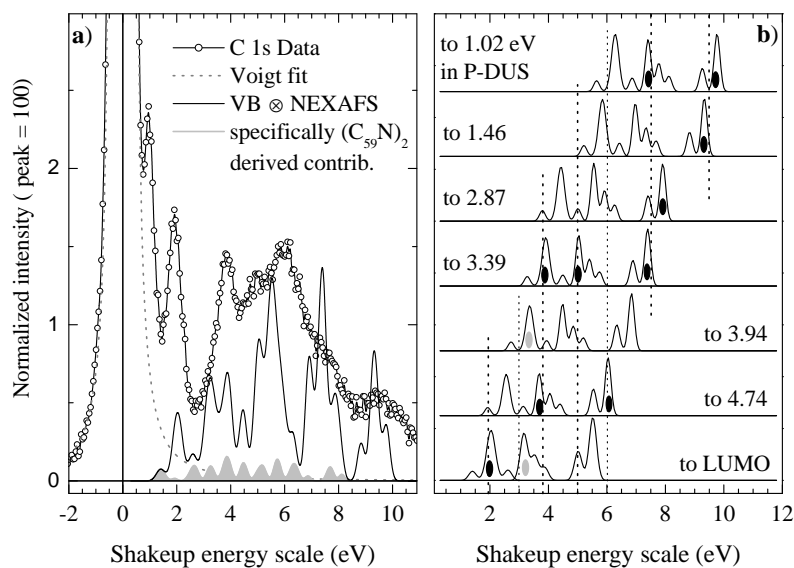


Figure 3. a) $(C_{59}N)_2$ carbon 1s and shake-up, after subtraction of a Shirley background. The VB-NEXAFS convolution is printed underneath. The shaded spectrum indicates the contribution of the three shaded peaks in Fig. 1. b) Convolution of all VB peaks with single peaks from the NEXAFS spectrum as indicated. The black (grey) dots mark strong (weaker) contributors to shake-up structures - indicated by vertical lines - found for C_{60} .

Gaussian, which peaks at 5.26 eV. The full widths at half maximum (FWHMs) of the Gaussians vary between 0.19 and 0.34 eV, apart from the 1.02 eV peak which has a FWHM of 0.44 eV due to its closer proximity to the unbound states above the vacuum level. In the valence band spectrum the $(C_{59}N)_2$ HOMO sits at 6.37 eV and FWHMs here range from 0.19 to 0.36 eV, with the exception of those at 7.0 eV (corresponding to the C_{60} HOMO) and 10.48 eV which have FWHMs of 0.42 and 0.62 eV respectively, indicating that they could consist of several closely spaced levels.

We now turn our attention to the C 1s core level spectrum in Fig. 3a (obtained at $h\nu = 350$ eV). The main peak at 289.70 eV (referenced to the vacuum level) is symmetric and has a FWHM of 0.47 eV. This is closer to the 0.35 - 0.5 eV FWHM of C_{60} previously observed [7, 9] and both narrower and more symmetric than the 0.7 eV reported for $(C_{59}N)_2$ [9]. We believe this might be due to the use of a lower photon energy and, possibly, the growth of a more homogeneous film. It can be represented by a single Voigt peak with a Gaussian width of 0.40 eV, and a Lorentzian width of 0.10 eV. Importantly, the narrow main line allows us to resolve the shake-up features in clear detail, and significantly, reveals a new sharp feature at 1.05 eV, at a relative total integrated intensity of 1:90 compared to the main peak. The rest of the shake-up features have an almost one-to-one correspondence with those in C_{60} [8, 9]. To investigate the origin of this new peak, we have constructed a qualitative shake-up spectrum. This, we believe, can be established by using the fits to the VB and NEXAFS spectra, and taking their convolution. This should give a reasonably accurate representation of the energy positions of the *on-site* shake-up spectrum as the NEXAFS data represent the unoccupied states *in the presence of a core hole*, and the valence band is close to the ground state density of states (DOS). The only effect not taken into account is the effect of the core hole on the DOS of the valence band. In addition, since the convolution relies solely on the energy separation between the occupied and unoccupied states, any rigid shift needed to align the convolution with the shake-up structures can provide additional information regarding delocalization. We do not expect, of course, the *intensities* of the calculated spectrum to be accurate, since this convolution does not encompass the appropriate (mostly monopole) matrix elements. Rather than using the original spectra (which gives broad shake-up structures) we use the fitted Gaussians instead. This allows us to reduce the widths of the peaks (set to 0.1 eV) and to emphasize the similarity to C_{60} by tuning their amplitude (1 for strong C_{60} -like peaks, 0.5 for intermediate and 0.25 for weak features and

the three $(C_{59}N)_2$ features of the VB). From Fig. 3a the qualitative agreement of the convolution with the measured shake-up spectrum is evident, and apart from the 1 eV feature, all the peaks are present and correspond well in energy after a rigid shift of 0.3 eV. This makes the first, small grey peak correspond to the onset of the optical spectrum at 1.4 eV [9, 10]. The peak close to 3 eV in our convoluted spectrum is due to an excitation from the C_{60} -like HOMO-1 level into the LUMO and is observed in reflection EELS, but its dipole-forbidden character makes it weak in other experiments [10, 8]. The π -plasmon also contributes strongly to the feature at 6 eV. Probable origins for the different shake-up structures are further clarified in Fig. 3b, in analogy to C_{60} 's shake-up structures [8]. As a consequence of these assignments, an excitonic origin for the 1 eV peak now seems unlikely. Although it is not entirely impossible to envisage a charge transfer exciton involving the outermost nitrogen electron clocking up a net energy gain of 0.35 eV in the presence of a core hole, another possibility cannot be overlooked: the difference in C 1s binding energy (BE) for an sp^2 carbon bound to either 3 carbons, or to 2 carbons and 1 nitrogen, is of the order of 1 eV [11, 12]. Similarly, the BE difference between *pure* sp^2 and sp^3 carbon is also of the same order [13, 14]. In $(C_{59}N)_2$ both these carbon bonding alterations are present. However, since the only sp^3 -like carbon in $(C_{59}N)_2$ is *also* bound to a nitrogen atom, we could therefore expect a BE shift in excess of 1 eV for that atom. This brings us to conclude that we can most likely attribute the 1.05 eV peak to the two sp^2 -like C atoms that are bound to 1 nitrogen and 2 carbon atoms [15].

Acknowledgments

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