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THE ELECTRONIC STRUCTURE OF $C_{59}N$ AND ITS $A_xC_{59}N$ ($A=K, Rb, Cs$) SALTS FROM HIGH ENERGY SPECTROSCOPY

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ABSTRACT

Using a combination of results from photoemission, electron energy-loss spectroscopy in transmission and gradient-corrected density functional calculations, we have examined the effects of chemical substitution of N for C in the dimerised heterofullerene $(C_{59}N)_2$. We show that there is a new HOMO state, which lies close in energy to the h_u -states of C_{60} and has a significant degree of N-character. In contrast, the lowest lying unoccupied levels have predominantly C-character.

The photoemission data of the alkali metal intercalated salts $A_xC_{59}N$ reveal signs of at least one additional phase other than the undoped $(C_{59}N)_2$ and an alkali metal saturated phase. At no stage during the intercalation is experimental evidence for metallic behaviour (in the form of a density of states at the Fermi level) observed.

1 Introduction

Heterofullerenes represent the third possible method of permanently altering the charge state of fullerene molecules after exohedral (intercalation) and endohedral doping. Up until recently, however, the heterofullerenes in the form of $C_{59}N$ and $C_{59}B$ have remained exotic members of the fullerene family only to be found in molecular beams [1]. Calculations of the electronic structure of $C_{59}N$ and $C_{59}B$ monomers [2] predicted an electronic behaviour similar to that of deep donor and acceptor levels in doped semiconductors.

The breakthrough came with the development of an organic synthetic route to the heterofullerene $C_{59}N$ [3]. Thus since 1995, pure $C_{59}N$, which is stable as a dimer, has been available in bulk quantities. X-ray diffraction studies of pristine $(C_{59}N)_2$ solid determined a monoclinic unit cell [4] with parameters close to those of the dimeric phase of Rb_1C_{60} .

Here we report the investigation of the electronic structure of both the pristine heterofullerene $(C_{59}N)_2$ as well as alkali metal intercalated $A_xC_{59}N$ using photoemission spectroscopy (PES) and electron energy-loss spectroscopy (EELS) in transmission. In addition, comparison of the experimental data with density functional calculations sheds additional light on the nature of the 'on-ball' doping in the pristine heterofullerene.

2 Experimental

After degassing $(C_{59}N)_2$ (200° C for 48 h), thin films were prepared in ultra high vacuum by sublimation at 560° C onto freshly evaporated gold films (PES) and KBr single crystals (EELS). Alkali metal doping was performed *in situ* using commercial SAES getter sources. During the doping process the sample was kept at 100° C and additional annealing at 150° C was performed to further improve homogeneity. For the EELS measurements, free-standing films were prepared [5] and the measurements were performed using a spectrometer described elsewhere [6]. Two different sets of energy and momentum resolution were chosen for the core level excitation measurements: 340 meV and 0.12 Å⁻¹ (N1s) and 160 meV and 0.1 Å⁻¹ (C1s). Electron diffraction gave diffraction patterns consistent with the reported structures [4,7]. For PES, the film thickness was ~ 100 Å, and the spectra were recorded using a He discharge lamp ($h\nu=21.22$ eV) and a commercial electron energy analyser. An energy resolution of 150 meV was chosen and the data were corrected for contributions from He satellite radiation.

The DFT-based calculations of the electronic structure were performed for isolated molecules of $(C_{59}N)_2$ using gradient-corrected exchange and correlation functionals [8].

3 Results and discussion

The results from pristine dimerised $C_{59}N$ are depicted in Fig. 1. In the upper panel are plotted the valence band photoemission spectrum, EELS C1s core level excitation spectrum and EELS N1s excitation spectrum - the latter shifted by the difference between the measured N1s and C1s XPS binding energies (BE's) of $(C_{59}N)_2$. The spectra are normalized to the intensity of the *s*-derived structure at 5.5 eV BE (PES) and to the *s** onset at 290.5 eV (EELS). These measurements give, as it is well known, a measure of the occupied (PES) and the site specific unoccupied electronic structure (EELS core level excitations, neglecting effects of the core hole). At the bottom of Fig. 1, we show the calculated total density of states (DOS) and the DOS projected onto the N-derived states (labelled N-PDOS) [9], both appropriately broadened to account for lifetime effects and finite spectrometer resolution. The agreement between experiment and theory is striking.

Compared to C_{60} (not shown), the PES and the C1s excitation spectra of the heterofullerene are slightly broadened, with the main structures appearing at roughly

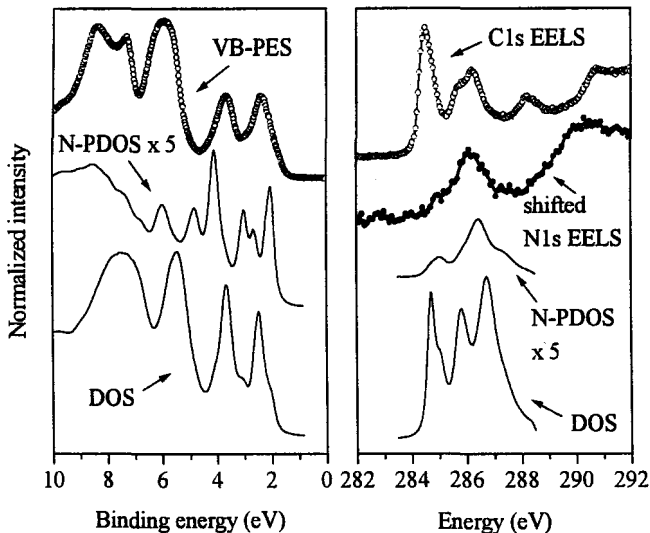


Fig. 1 : Valence band photoemission spectrum (o), C1s core level excitation spectrum (o) and N1s excitation spectrum [(•) shifted by the difference of the N1s and C1s XPS BE] of $(C_{59}N)_2$. In the lower part of each panel are the calculated densities of states (DOS) and calculated DOS projected onto the N-derived states (N-PDOS) broadened for lifetime effects and finite spectrometer resolution.

the same energies [9]. Comparison of the data from the heterofullerene with the N-PDOS reveals the atomic character of the PES spectrum at about 1.9 eV, 2.8 eV, and 4 eV BE. In particular, the shoulder at 1.9 eV BE, which contains the HOMO of the $C_{59}N$ dimer, has strong N-character. In fact, this molecular orbital has the majority of its electronic density at the N atoms and the intermolecular bond of the dimer [9]. In contrast, the comparison of the N1s excitation spectrum to the N-PDOS confirms that the lowest group of unoccupied electronic levels has only a small weight at the N atoms and is therefore mainly C-derived.

We now turn to the alkali metal intercalated $C_{59}N$ (the archetypal heterofulleride). At present, $K_6C_{59}N$ is the only heterofullerene salt to have been prepared in a phase-pure form and to have been fully structurally characterised [7]. From this it is known that $K_6C_{59}N$ is isostructural with bcc K_6C_{60} - and that the heterofullerene molecules are present as monomers. In bulk samples of the $A_6C_{59}N$ materials, the 'extra' electron (in comparison with A_6C_{60}) appears to be localised, resulting in a Curie-Weiss-like susceptibility (giving a moment of $\sim 0.4\text{-}0.5 \mu_B$ per $C_{59}N$ monomer) [10].

Here, the electronic structure of $A_xC_{59}N$ has been studied using PES as a function of intercalation for $A = K, Rb,$ and Cs . In all three cases we find (except for a slightly different width of the features) very similar spectra. In Fig. 2, as an example of the

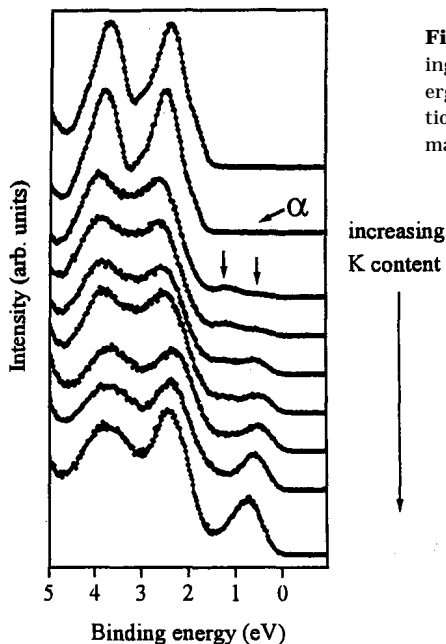


Fig. 2: PES spectra of $K_xC_{59}N$ with increasing potassium intercalation. The two low energy features which appear upon intercalation are marked with arrows. The α phase is marked.

general $A_xC_{59}N$ behaviour, the PES spectra of $K_xC_{59}N$ are plotted for increasing potassium intercalation. The spectrum for very low K content resembles that of the solid solution 'a phase' in the $K-C_{60}$ system. In this case, E_F is pinned at the onset of the LUMO, thus resulting in a 0.2 eV shift of the $(C_{59}N)_2$ spectrum to higher BE. Consequently, the gap observed for the a phase in PES (1.4eV) corresponds to the so-called 'transport-gap' (onset-onset) of $C_{59}N$ dimer. Interestingly, this is the same size as the optical gap observed in EELS experiments [11], indicating an apparent complete lack of excitonic effects in the latter. This is in contrast to the situation in C_{60} .

Upon increasing intercalation, an additional feature at about 1.2 eV BE appears, which then gives way on further intercalation to a second, broad structure at a binding energy of ~ 0.5 eV. As intercalation progresses further, this second structure grows in weight and shifts to higher BE, situated at some 0.7eV for the potassium saturated sample. This shift of the spectral weight of the now occupied LUMO to higher BE upon alkali saturation is reminiscent of the situation in K_6C_{60} [5]. Attempts to intercalate further lead to formation of an alkali metal film on the sample surface which then oxidises rapidly (and is thus easily experimentally identified). We note that at no stage during intercalation do we observe a DOS at E_F indicative of metallic behaviour.

The observed PES profiles are consistent with the presence of at least one phase (leading to the peak observed at 1.2eV BE) other than the end-members in the

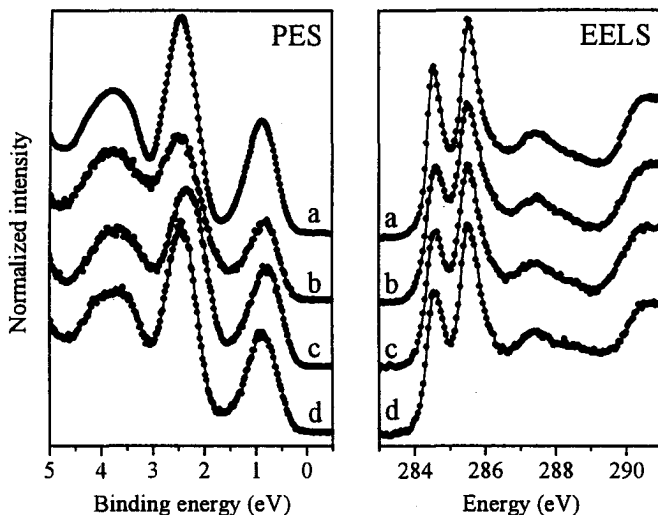


Fig. 3: PES spectra and EELS C1s excitation spectra of (a) K_6C_{60} , and the alkali metal (A) saturated films of $C_{59}N$: (b) $A=K$ (c) $A=Rb$ and (d) $A=Cs$. All spectra are normalized to the area up to 5 eV BE and to the s^* edge at 290.5 eV.

$A-C_{59}N$ systems ($A = K, Rb$ and Cs). In other words, we find a similar situation to that of A_xC_{70} ($A = Rb$ [5], K [12]), where no evidence for any density of states at E_F indicating a metallic intermediate phase is observed. This serves to emphasize the exceptional nature of the A_3C_{60} materials - indicating perhaps a vital role played by the high symmetry (and thus high degeneracy) in this system.

Fig. 3 shows the comparison of the PES spectra and EELS C1s excitation spectra of K_6C_{60} and the alkali metal saturated C_{59} films with $A = K, Rb$ and Cs . It is evident that apart from a small broadening, all the spectra of the heterofullerene salts look very similar to those of K_6C_{60} . From the EELS C1s edges, probing the unoccupied electronic structure, the LUMO-derived feature at 284.8 eV can be seen to be slightly reduced in intensity in the heterofullerides. However a quantification of the reduced p^* density in the LUMO requires further investigation.

The similarity of the C1s excitation spectra of the highly intercalated $A_xC_{59}N$ with that of K_6C_{60} bears out the conclusion arrived at earlier that the lowest group of unoccupied electronic levels in the heterofullerene are of almost pure C-character.

Application of the same procedure as used here to produce the alkali metal saturated $C_{59}N$ films to C_{60} yields A_6C_{60} samples. Thus if the heterofullerene's intercalation chemistry were the same as that of its unsubstituted cousin, then the saturated $C_{59}N$ films studied here would be $A_6C_{59}N$, and would thus possess an additional electron in comparison with K_6C_{60} . However, in this case, one would expect to find some signs of a singly occupied molecular orbital in the high energy spectroscopic data of

the heterofullerides [13]. Thus, at this stage, the strong resemblance of the saturated heterofulleride data with those of K_6C_{60} remains a puzzle.

To summarize, we have analysed the occupied and unoccupied electronic structure of the pristine and intercalated heterofullerene $C_{59}N$. We show that the pristine heterofullerene dimer has a new HOMO, which has large weight at the N-atoms and on the intermolecular bond, whereas the LUMO has only very little N-character. Upon alkali metal intercalation, we find evidence from PES for at least one intermediate phase between the end members. None of the phases achieved in the $A-C_{59}N$ system ($A=K, Rb, Cs$) appear to be metallic, as seen by photoemission. For the fully alkali metal saturated $C_{59}N$ compounds, we observe both PES and EELS $C1s$ excitation spectra which are surprisingly similar to those of K_6C_{60} .

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