On-Ball Doping of Fullerenes: The Electronic Structure of $C_{59}N$ Dimers from Experiment and Theory

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We present the first studies of the electronic structure of the heterofullerene $(C_{59}N)_2$ using electron energy-loss spectroscopy in transmission, photoemission spectroscopy, and density functional theory calculations. Both the C 1*s* excitation spectra and valence band photoemission show negligible occupation of the C-derived lowest unoccupied electronic states and indicate localization of the excess electrons at the N atoms. The experimental results, together with the detailed analysis of our theoretical data, provide compelling evidence for the chemical picture of a triply coordinated N atom with a lone pair in each heterofullerene unit, and confirm the theoretically predicted "6,6 closed" structure for the dimer. [S0031-9007(97)03216-X]

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There are three conceivable methods of permanently altering the charge distribution and electronic structure of fullerenes in the solid state: the introduction of dopant species surrounding the fullerene molecules (intercalation), the inclusion of atoms or ions inside the fullerene cage (endohedral fullerenes), or the substitution of one or more of the carbon atoms with heteroatoms. The preparation and mass spectroscopic identification of such heterofullerenes was already reported as early as 1991 [1]. Shortly thereafter, the electronic structure was calculated for $C_{59}N$ and $C_{59}B$ monomers [2]. An electronic behavior similar to that of deep donor and acceptor levels in doped semiconductors was predicted. However, only since the synthesis and isolation of bulk quantities of the heterofullerene $C_{59}N$ [3] has it been possible to investigate the physical and chemical properties of these newest members of the fullerene family. Based on a series of physical and chemical data it was concluded that $C_{59}N$ is stable as a dimer, for which two configurations were originally proposed: the so-called "6,6 closed" and "6,6 open" structures [3]. The crystal structure of pristine $(C_{59}N)_2$ solid has been determined [4,5], confirming the dimerized nature of the heterofullerene which crystallizes in a monoclinic cell [6] with parameters close to those of the dimeric phase of Rb_1C_{60} [7]. Recent density functional theory (DFT) calculations also find a dimerized structure for the heterofullerene, with only one C-C intermolecular bond and C_{2h} symmetry. The N atoms are predicted to be in a *trans* configuration, with a "closed" C- N network on the ball [8]. This structure is very similar to the molecular configuration of isoelectronic dimerized $C_{60}{}^-$, as obtained from both calculations [8,9] and experiment on Rb_1C_{60} [7].

In this Letter, we report the first investigation of the electronic structure of a heterofullerene $(C_{59}N)_2$, which can be thought of as *n*-type on-cage doped C_{60}, using both photoemission spectroscopy (PES) and electron energy-loss spectroscopy (EELS) in transmission. Comparison with C_{60} and with our DFT calculations reveals that the extra electron does not occupy the lowest-lying C-derived states, but can be described as forming part of a lone pair on the nitrogen, which interacts with the nearby carbon atoms. N 1*s* excitation spectra are also used to probe the chemical bonding on the ball, and confirm the theoretically predicted molecular structure. Further comparison of $(C_{59}N)_2$ with the isoelectronic dimer phase of Rb_1C_{60}, carried out both experimentally and theoretically, shows that the role of the extra core charge at the nitrogen site is vital in understanding the differences between the spectra of the on-ball-doped and intercalation-doped dimers.

After degassing of $(C_{59}N)_2$ in ultrahigh vacuum at 200 °C for 48 h, thin films were prepared by subliming at 560 °C onto freshly evaporated gold films (PES) and KBr single crystals (EELS). Mid-infrared and optical absorption spectroscopy showed no signs of remaining solvent, C_{60}, or other contamination. For the EELS measurements, free-standing films with a thickness of about 1000 Å were prepared by dissolving the KBr substrate in distilled water. The measurements were performed using a spectrometer described elsewhere [10]. Two different sets of energy and momentum resolution were chosen for the core level excitation measurements: 340 meV and $0.12\,\text{Å}^{-1}$ (N 1*s*) and 160 meV and $0.1\,\text{Å}^{-1}$ (C 1*s*). Electron diffraction studies both in the EELS spectrometer and in a

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transmission electron microscope gave diffraction patterns consistent with the reported monoclinic structure [6]. 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 analyzer. An energy resolution of 150 meV was chosen, and the data were corrected for contributions from He satellite radiation.

Our DFT-based calculations of the electronic structure were performed for isolated molecules of $(C_{59}N)_2$ using gradient-corrected exchange and correlation functionals [11]. Here we discuss the density of the occupied and unoccupied one-electron states (DOS), as well as its projection onto the nitrogen atomic functions (N-PDOS).

It is well known that levels derived from such calculations do not correspond to quasiparticle excitation energies [12]. However, the DOS generally reproduces the photoemission spectra of fullerenes reasonably well and in particular their salient features in the range of a few eV below the Fermi level [13].

Figure 1 shows a comparison of the valence band photoemission spectra (left panel) and the C 1*s* excitation spectra (right panel) of $(C_{59}N)_2$ and C_{60}. These measurements give a measure of the occupied (PES) and site specific unoccupied (EELS core level excitations neglecting effects of the core hole) electronic structure. The data are normalized to the intensity of the σ-derived structure at 5.5 eV binding energy (BE) and to the $\sigma^\star$ onset at 290.5 eV. In addition, the right panel of Fig. 1 shows the N 1*s* excitation spectrum of $(C_{59}N)_2$ downshifted in energy by 115.5 eV, which is the difference between the N 1*s* and C 1*s* core level binding energies ($400.7 - 285.2 = 115.5$ eV), measured using x-ray photoemission (data not shown). At the bottom in each panel, the calculated N-PDOS and the total DOS are plotted. For the purpose of comparison, the discrete levels of the isolated dimer were broadened so as to simulate solid state effects as well as lifetime and spectrometer resolution broadening, and the DOS were shifted such that the energy of the leading maximum matches that observed in experiment. For $(C_{59}N)_2$, both the PES and C 1*s* excitation spectra are broader than those of C_{60}, but the energy positions of the main features are unchanged. Additionally, the first photoemission maximum of $(C_{59}N)_2$ has a shoulder at about 0.5 eV lower BE, which, upon consideration of the N-PDOS, can be assigned to states related to the extra electron which maintains a high degree of nitrogen character. This conclusion is supported by the electron density distribution of the highest occupied molecular orbital (HOMO) of $(C_{59}N)_2$ shown in Fig. 2(a). It is clear from the figure that this HOMO is different to that of C_{60}, with the electron density strongly concentrated on the N atoms and along the axis of the intermolecular bond.

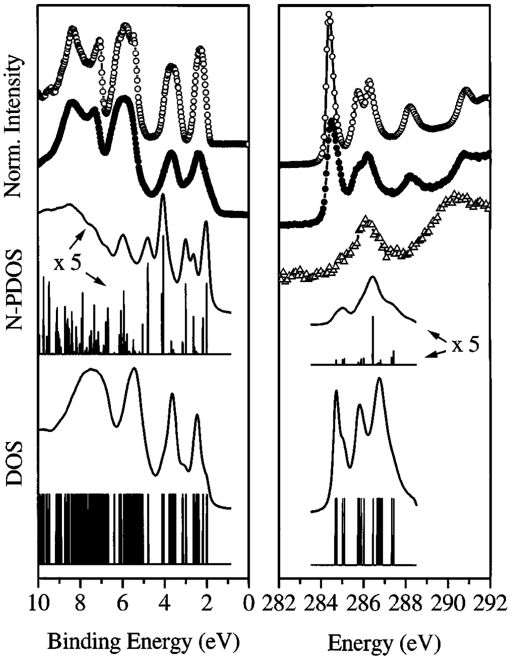

FIG. 1. Valence band photoemission spectra and C 1*s* core level excitation spectra of $(C_{59}N)_2$ (•), and C_{60} (○). Also shown is the N 1*s* excitation spectrum (△) of the heterofullerene. At the bottom in each panel are both the calculated densities of states (DOS) and the broadened DOS for the $C_{59}N$ dimer and the DOS projected onto the N atomic functions (N-PDOS).

The overall shape of the C 1*s* excitation spectrum of the heterofullerene (Fig. 1) is very similar to that of C_{60}, apart from an extra broadening of the spectral features of the former. In fact, within experimental error, the spectral weight of all $\pi^\star$-derived structures below the $\sigma^\star$ edge at 292 eV is identical for both C_{60} and the heterofullerene. This indicates that the N substitution does not lead to significant occupation of the C-derived low-lying unoccupied states of C_{60}. The lack of a strong feature in the N 1*s* excitation spectrum at energies corresponding to the lowest unoccupied states in the C 1*s* spectrum also lends weight to the arguments put forward above in favor of the localization of the "extra" electron. This is fully supported by the calculated unoccupied N-PDOS (Fig. 1), and by the density distribution of the lowest six unoccupied states of the heterofullerene (spanning a range of 0.4 eV in the molecule) shown in Fig. 2(b). Note that these orbitals are mainly the t_{1u}-derived states of C_{60} and have weak amplitude on the intermolecular bond.

It is instructive not only to compare the results from $C_{59}N$ to those of C_{60}, but also to those of the isostructural and isoelectronic C_{60}^- dimers in quenched Rb_1C_{60}. Figure 3 shows such a comparison for the PES spectra of $(C_{59}N)_2$ and Rb_1C_{60} (data from Ref. [14]) up to a BE of 5 eV. For the purposes of comparison, the spectrum of dimerized Rb_1C_{60} has been shifted by 0.25 eV to lower BE. From the PES spectra shown in Fig. 3, it would appear that the perturbation of the electronic levels of C_{60} is more pronounced in the case of the Rb_1C_{60} dimer—with the photoemission feature at highest energy clearly

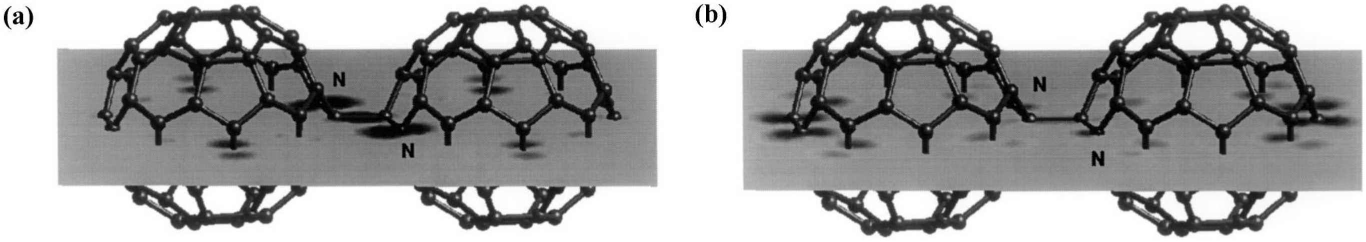

FIG. 2. A cut through the electronic density distribution of (a) the HOMO (left panel) and (b) the LUMO (right panel) of $(C_{59}N)_2$ depicted in the plane passing through the N atoms and the intermolecular bond.

consisting of two peaks separated by ~0.3 eV, and split-off from the rest of the spectrum by ~1 eV. Based on the behavior of other alkali metal fullerides [13], one can reasonably expect the charge transfer from the Rb 5*s* states to be complete, and thus we compare the PES spectrum of Rb_1C_{60} with the broadened DOS of the isolated C_{60}^- dimer (Ref. [8]). The energy distribution of the states observed in the PES spectra of the solids is well reproduced in the calculation, apart from a smaller separation of the highest energy feature from the main peak in the case of the C_{60}^- dimer. This type of discrepancy can be expected as a result of the difference between a free molecular anion and one confined in the solid fulleride. Our calculations show that the spatial distribution of the HOMO in the C_{60}^- dimer is as pictured in Fig. 2(a), with the largest amplitude on the C atoms in the positions corresponding to the nitrogens in $(C_{59}N)_2$.

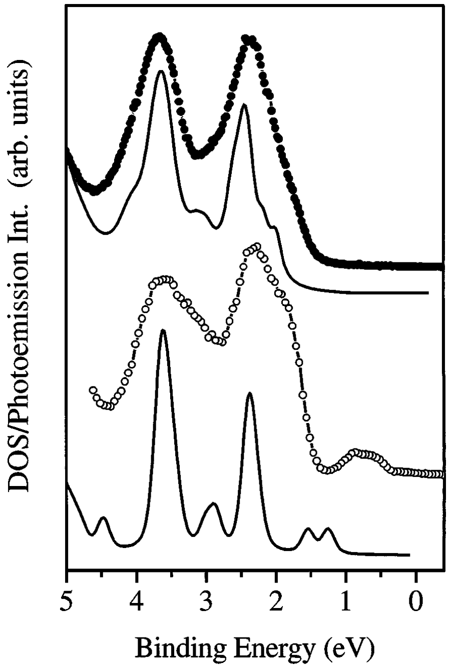

FIG. 3. Valence band photoemission spectra of $(C_{59}N)_2$ (•) and $(Rb_1C_{60})_2$ (∘) (spectra of the latter from Ref. [14]). The spectrum of dimerized Rb_1C_{60} is shifted by 0.25 eV to lower binding energy. The solid lines are the calculated DOS for a $C_{59}N$ dimer and for a C_{60}^- dimer, respectively. For details, see text.

The most important difference between the two dimers is due to the presence of the additional positive charge on the nitrogen cores in the heterofullerene. This causes a lowering of the energy of the HOMO and HOMO-1 states of the $C_{59}N$ dimer and reduces the splitting of the occupied electronic levels in general.

Measurements of the N 1*s* excitation edge can also be used as a probe of the chemical environment of the nitrogen atom in the heterofullerene. Figure 4 shows a comparison of the N 1*s* excitation edge of the heterofullerene with those of two conjugated carbon systems containing nitrogen atoms which can serve as models of the nitrogen coordination in $C_{59}N$ [10]. In polypyrrole (PPY), despite the fact that one neighbor is a hydrogen atom, the nitrogen is in a configuration similar to that in the "6,6 closed" dimeric structure—i.e., with three neighbors and possessing a lone pair. In contrast, in polymethineimine (PMI) or deprotonated PPY, [10] the nitrogen has only two neighbors (similar to the "6,6 open" configuration of the

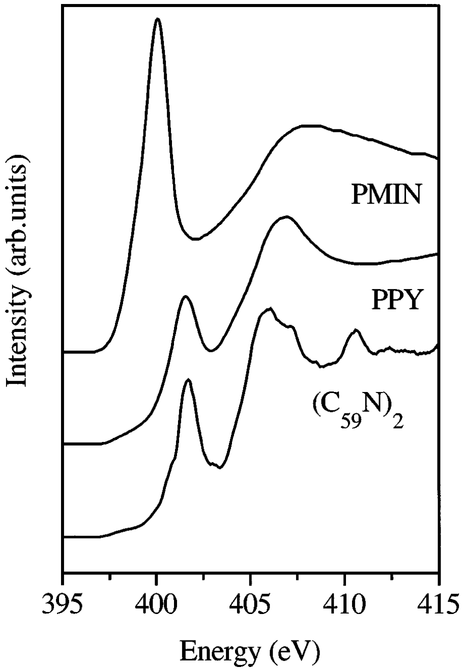

FIG. 4. Comparison of the N 1*s* excitation spectra of dimerized $C_{59}N$, polypyrrole (PPY) [10] and polymethineimine (PMI) [10].

heterofullerene), leading both to additional charge on the nitrogen and a different orbital character of the lone pair. As can be seen from Fig. 4, the N 1*s* excitation spectrum of the heterofullerene closely resembles that of PPY, thus providing compelling evidence for the "6,6 closed" structure, in agreement with theoretical predictions [8].

In conclusion, we have carried out the first experimental and theoretical investigation of the electronic structure of the on-ball doped heterofullerene $C_{59}N$. We show that the extra electron in the heterofullerene is predominantly localized on the N atom. This results in only a weak perturbation of both the occupied and unoccupied C-derived states. The overall picture matches one of a triply coordinated N atom with a lone pair. Our calculations show that the nature of the HOMOs of the $C_{59}N$ and $C_{60}{}^{-}$ dimers is very similar; however, the additional core potential at the nitrogen results in both a lowering of the energy of the HOMO and in a strongly reduced splitting of the occupied electronic levels in the heterofullerene. In addition, we also provide strong experimental evidence for the "6,6 closed" structure, in addition to evidence based on the parent $C_{59}HN$ [15].

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