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Final-state interference effects in valence band photoemission of $(C_{59}N)_2$ Michael R. C. Hunt,^{1,2} Thomas Pichler,^{3,4} Lidija Šiller,⁵ Paul A. Brühwiler,⁶ Mark S. Golden,^{3,*} Nikos Tagmatarchis,^{7,†} Kosmas Prassides,⁷ and Petra Rudolf¹¹*LISE, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium*²*School of Physics and Astronomy, The University of Nottingham, Nottingham NG7 2RD, United Kingdom*³*IFW Dresden, D-01171 Dresden, Germany*⁴*Institute of Materials Physics, University of Vienna, A-1090, Vienna, Austria*⁵*Department of Physics, The University of Newcastle, Newcastle upon Tyne, NE1 7RU, United Kingdom*⁶*Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden*⁷*School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, United Kingdom*

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Oscillatory behavior of photoemission intensity with incident photon energy has been observed for several fullerenes and fullerene derivatives. However, until now it has been unclear if these effects arise from interference associated with the spatial distribution of the initial state within the molecule or are due to scattering of the outgoing photoelectron. In order to resolve this issue we performed synchrotron radiation excited valence band photoemission measurements on multilayer $(C_{59}N)_2$ films. The highest occupied molecular orbital (HOMO) of the $(C_{59}N)_2$ dimer is spatially localized, while each half of the dimer remains approximately spherical. Careful normalization and fitting of the measured spectra clearly show that the intensity of the HOMO also displays a periodic variation of intensity with photon energy indicating that scattering of the photoemitted electron and consequent interference effects lead to the observed intensity changes.

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A particularly interesting feature arising in photoemission from the fullerenes is the observation of an oscillatory change in photoemission intensity from the valence band states as a function of incident photon energy. First observed in solid films of C_{60} ,¹ these intensity modulations have been observed in gas phase C_{60} (Ref. 2) and C_{70} ,³ as well as in films of $(C_{59}N)_2$ (Ref. 4) and of higher fullerenes.⁵ An almost antiphase oscillation in the intensity of the first two valence band features of C_{60} was observed by Benning and co-workers.¹ Both these states have π -orbital character and differ only in parity and angular momentum, and it was suggested that the photoelectron final state retained molecular character in the form of parity for energies as high as 120 eV above the vacuum level. Subsequent calculations^{6–9} have suggested that intramolecular interference effects may be the dominant factor in determining the measured intensities. Several similar models have been formulated which can be classified in two groups, one in which the phase difference across the molecule of the photoemission *initial state* is deemed to be important,^{6–8} the other in which scattering of the *final state* wave function by the molecule⁹ determines intensity in a similar fashion. In both types of model a standing wavefield within the spherically symmetric “shell” of a fullerene is created. In the initial state model this arises from interference of a coherent spherically symmetric wave emitted from the shell itself, while for a final state model scattering of a photoelectron from the quasi-spherically arranged atoms of the shell produces the standing wave—effectively photoelectron diffraction. Consequently, in the first group of models increasing localization of the initial state wavefunction should have a profound, and destructive, effect upon the intensity variation with incident photon energy. For the second type of model localization of the initial state will have little, if any, effect on the observed oscillations in photoemission intensity.

Azafullerene,¹⁰ in which one carbon atom on C_{60} is substituted by a nitrogen atom, offers a unique opportunity to probe these effects of localization of the initial state in the photoemission process. The azafullerenyl radical $C_{59}N\cdot$ can be stabilized by reacting with hydrogen to form $C_{59}HN$,¹¹ by bonding to a semiconductor¹² or a metal¹³ surface or by forming dimers. $(C_{59}N)_2$ is stable in solution as well as in the solid phase where the dimers arrange in a monoclinic lattice.¹⁴ It is the dimerization in the solid phase which leads to the localization of the highest unoccupied molecular orbital (HOMO).^{15,16}

We explored intensity oscillations in the valence band of solid $(C_{59}N)_2$ at the I311 undulator beamline¹⁷ at the MAX II storage ring at MAX-lab in Lund, Sweden which was equipped with a modified SX-700 monochromator and a hemispherical SCIENTA SES 200 analyzer. The spectra were recorded at 96 K with a total (photons+electrons) energy resolution of 45 meV as determined from the width of the Fermi edge of the graphite substrate, measured at 96 K after cleaving in air and repeated heating under ultra high vacuum to bright orange glow to remove contaminants. $C_{59}N$ was synthesized and purified as described in Ref. 10. From IR measurements a C_{60} contamination of less than 1% was deduced for this material.¹⁸ $(C_{59}N)_2$ multilayer films were deposited *in situ* by sublimation from a boron nitride crucible onto the clean graphite (0001) kept at room temperature. Deposition at this temperature favours island growth as evidenced by the fact that the graphite Fermi edge was still visible when more than a nominal two monolayers of azafullerene were deposited. C_{60} multilayer films were produced the same way but using commercially available material (99.9% purity, MER Corporation) evaporated from a resistively heated Ta crucible. The pressure in the UHV chamber rose from 2×10^{-10} mbar to the low 10^{-8} mbar

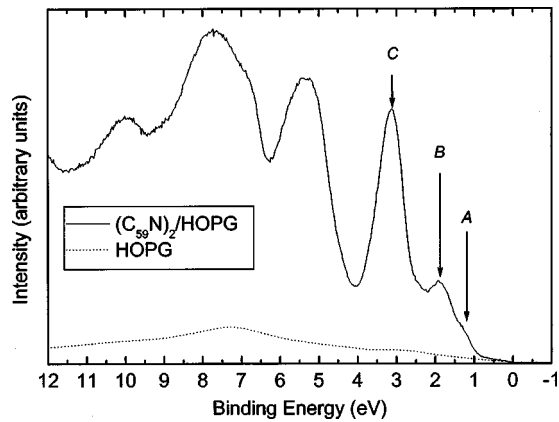


FIG. 1. Valence band spectrum of $(C_{59}N)_2$ obtained in normal emission geometry at a photon energy of 35 eV. The contribution from the graphite substrate is shown by the dotted line.

range during fullerene deposition. The cleanliness of the films was verified using core level photoemission.

Figure 1 shows a typical valence band photoemission spectrum from a film of $(C_{59}N)_2$ on graphite (0001). The overall shape of the spectrum is somewhat similar to that of a C_{60} multilayer, with key differences associated with the presence of extra states from the substitutional doping with nitrogen, and the distortion of the monomer cages brought about by both substitution and dimerization.^{15,16} The HOMO of the $(C_{59}N)_2$ dimer (Fig. 1, peak A) has a high degree of $N2p$ character and lies above the $C2p$ -dominated states which would form the HOMO of pure C_{60} (Fig. 1, peak B). Calculations demonstrate that the $(C_{59}N)_2$ HOMO is spatially localized on the dimer in the region of the intermolecular dimer bond and on the adjacent nitrogen atom,¹⁵ while the HOMO-1 (peak B) is more delocalized.

Photoemission spectra as a function of photon energy are shown in Fig. 2. A similar variation with photon energy has

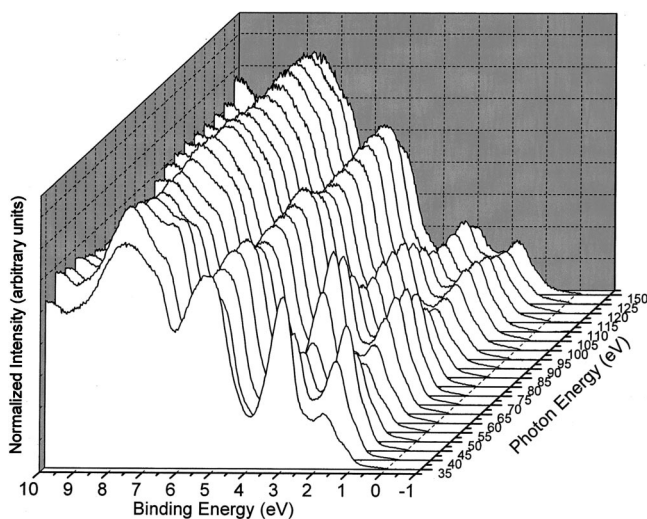


FIG. 2. Valence band spectra of $(C_{59}N)_2$ /HOPG showing oscillatory behavior of photoemission intensity as a function of photon energy. For a description of the normalization procedure see text. All spectra were obtained in normal emission geometry.

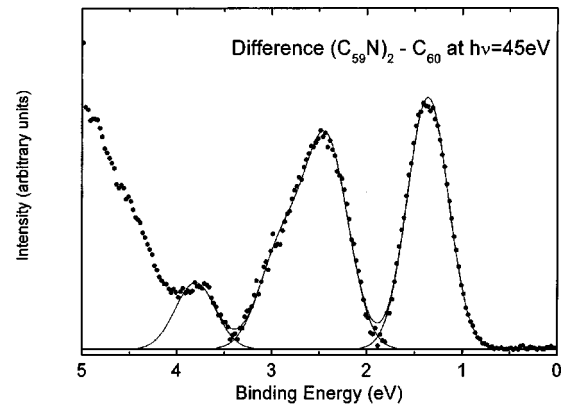


FIG. 3. Difference spectrum between the valence bands of C_{60} and $(C_{59}N)_2$ obtained at a photon energy of 45 eV (solid circles). The fit to the difference spectrum, shown as solid lines, was subsequently used as the basis of fits to the $(C_{59}N)_2$ valence band spectra as a function of photon energy, as described in the text.

been observed by Jones *et al.*⁴ However, only the first 5 eV of the valence band was reported in that work. Consequently, when the HOMO intensity was extracted by fitting it was normalized to the intensity of either peak B or C. Both peaks B and C undergo considerable intensity variations. Thus, the observed variation in the normalized intensity of the HOMO depended quite strongly upon the peak chosen for normalization. To eliminate these problems we have adopted a more rigorous normalization and fitting procedure. Spectra were taken over the binding energy range 12 to -1 eV. A residual signal from the graphite substrate, close to E_F was used to calibrate energy positions. In contrast to Ref. 4, no change in position of the valence band features was found with energy. Spectra were normalized to the total integrated spectral intensity over the binding energy range acquired. To ensure that the normalization procedure was sufficiently robust, spectra were also normalized to the incident photon flux and the final results of the normalization and fitting procedure found to be almost identical. The graphite background, normalized to the intensity near E_F was then subtracted from our spectra. Initial parameters for fitting were determined as follows: a valence band spectrum of multilayer C_{60} was obtained during the same beamtime under the same conditions as those for $(C_{59}N)_2$. A difference spectrum was then generated for $h\nu=45$ eV by subtracting the spectrum of multilayer C_{60} from that of $(C_{59}N)_2$, Fig. 3. The difference spectrum should reflect the additional density of valence band states associated with substitution of nitrogen into the fullerene cage and subsequent dimerization. Indeed, the resulting spectrum shows strong similarity to the N partial density of states (N-PDOS) of Ref. 15 formed by projecting the one electron states onto the nitrogen atomic functions. Although the difference spectrum contains intensity arising from the reduction in molecular symmetry and consequent broadening of other states, to a first approximation the leading feature is representative of the $(C_{59}N)_2$ HOMO. The difference spectrum was then fitted by a combination of three Gaussian functions (two singlets, one doublet) consistent with the theoretical N-PDOS (Ref. 15) as shown in Fig. 3.

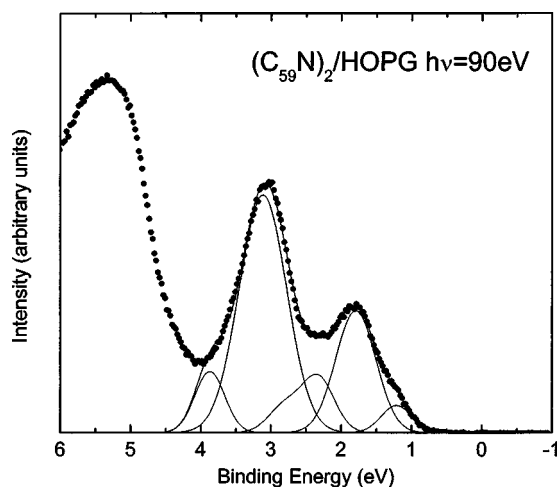


FIG. 4. Typical fit to a valence band photoemission spectrum of $(C_{59}N)_2$. The points correspond to the experimental spectrum, smooth lines to the fit and its components. For fit details: see text.

The normalized $(C_{59}N)_2$ spectra were then fitted with the sum of these functions and a pair of Gaussians obtained by fitting the leading features of the C_{60} valence band. Positions and intensities (including relative intensities in the doublet) were allowed to relax, but the relative positions and widths of the peaks generated by the difference spectrum were fixed. Figure 4 illustrates the high quality of typical fits resulting from this approach. It was found that extending the fit to include higher binding energy peaks did not lead to any significant changes in the intensities associated with the leading edge features. From these fits one can extract normalized areas associated with each of the peaks, which are plotted in Fig. 5. It is clearly seen that the areas of the peaks corresponding to the maxima A, B, and C (Fig. 1) display oscillatory intensity superposed on a decreasing background which arises from a reduction in the photoemission cross-section of p -orbital derived states with respect to the s -orbital derived states which play an important role in normalization. Although some small contribution to the oscillatory intensity observed in peak A may arise from overlap with peak B, the difference in the variation of the intensity of these peaks with photon energy is sufficient to draw the conclusion that the intensity of peak A varies nonmonotonically with photon energy. The presence of oscillations in the cross section of the $(C_{59}N)_2$ HOMO contradicts the assertion in Ref. 4 that no such oscillation could be detected.

If initial state effects are dominant in inducing the observed intensity oscillations⁶⁻⁸ then it can be expected that these would vanish if the initial state were spatially localized rather than distributed over the entire cage of a fullerene

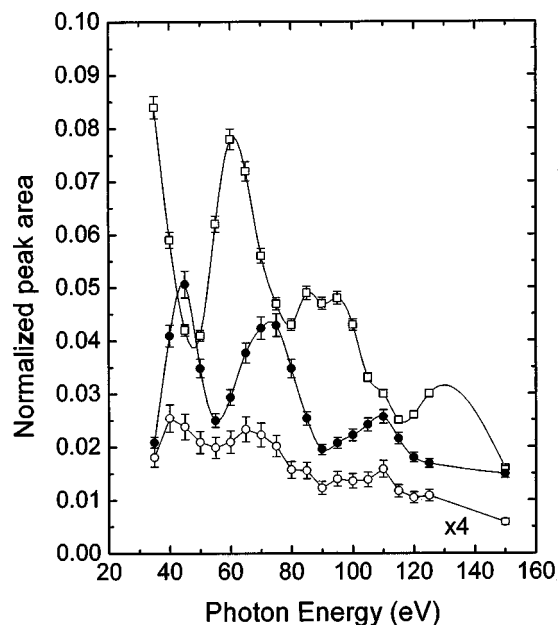


FIG. 5. Intensity oscillations of valence band features (integrated area) from $(C_{59}N)_2$ as a function of photon energy. Filled circles (●) correspond to the area of the fit peak centered at 1.8 eV, and open squares (□) to that at 3.1 eV, both of which are primarily $C2p$ derived (peaks B and C in Fig. 1). Open circles (○) correspond to the area of the fitted peak at 1.2 eV, which is primarily $N2p$ derived (shoulder A in Fig. 1). The solid lines are intended as a guide to the eye.

monomer or over the complete dimer. The continued presence of intensity oscillations for the $(C_{59}N)_2$ HOMO, which is rather localized within the dimer,^{15,16} indicates that interference effects associated with the passage of the photoelectron out of the molecules is primarily responsible for the intensity oscillations. Thus we can draw the conclusion that it is the scattering of the *outgoing* photoelectron from the quasispherical monomer components of the $(C_{59}N)_2$ dimer, and resulting interference effects which lead to the intensity oscillations observed as a function of photon energy for a number of fullerenes and fullerene derivatives.^{1-5,9}

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*Present address: Van der Waals-Zeeman Institute, University of Amsterdam, Vackenerstraat 65, NL-1018 XE Amsterdam, The Netherlands.

†Present address: Dipartimento di Scienze Farmaceutiche, Università degli Studi di Trieste, P.le Europa 1, I-34127 Trieste, Italy.

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