Oscillations in the valence-band photoemission spectrum of the heterofullerene $C_{59}N$: A photoelectron interference phenomenon

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The intensities of the two strongest low-binding energy features in the valence-band photoemission spectra of $C_{59}N$ have been observed to oscillate as the photon energy of the exciting radiation is varied. The maxima in the intensity ratio of the two peaks occur at the same photon energies as the maxima in the intensity ratios of the highest occupied molecular orbitals to next highest occupied molecular orbitals (NHOMO) peaks of C_{60}. The amplitude of modulation of the ratio is remarkably similar in both cases. Since the nature of the filled and empty states involved in the photoemission process are different for $C_{59}N$ compared to C_{60}, the current observation therefore supports the proposal that the final state is of negligible importance in the mechanism leading to the oscillations. The intensity variation instead arises from a photoelectron interference effect as a consequence of the spherical environment of the electron emitters within the molecule. [S0163-1829(99)02715-0]

An especially striking characteristic of the valence-band photoemission spectra of C_{60} is that the intensities of the peaks corresponding to electron emission from the highest and next-highest occupied molecular orbitals (the HOMO and NHOMO) show distinct oscillations as the photon energy of the incident radiation is varied.[1–6] First observed for condensed films,[1] essentially identical oscillations have subsequently been recorded from both single crystal[2] and gas phase[3] C_{60}. As a result, some discussion has arisen as to the origin of the phenomenon. It was initially proposed that the peak intensities are strongly dependent on the molecular nature of both the filled and empty states involved in the photoemission process. Assuming that the final states retain distinct molecular character up to energies of at least 100 eV above the HOMO, the oscillations can be explained qualitatively on the basis of the parity selection rule. However, calculations based on this model and free-electron-like final states were found to be inconsistent with the experimental results.[2]

Alternative approaches to an explanation of the effect have considered the interaction between the photoelectrons generated within the molecule. Xu, Tan, and Becker suggested that interference between the photoelectrons could create a spherical standing wave final state.[4] Most recently, however, Hasegawa *et al.* used *ab initio* calculations to determine the differential photoionization cross sections for the HOMO and NHOMO.[5,6] The derived cross sections were shown to depend upon the interference of the individual photoelectron waves emanating from each of the C atoms in the

C_{60} cage. It is important to note that Hasegawa *et al.* also approximated the initial state molecular orbital to a spherical shell-like state. The modulation of the differential photoionization cross section was still apparent even after this radical simplification, strongly suggesting that the spherical structure and relatively large radius of the C_{60} molecule are essential factors in causing the photoemission intensity oscillations.

To date, photon-energy-dependent oscillations in photoemission intensities have not been observed for any molecular solids other than C_{60}. However, the proposal of a model based on a photoelectron interference effect implies that other nearly spherical molecules with large radii should show similar effects in their photoemission spectra. In the current paper, we address this issue by examining changes in the valence region photoemission spectrum of the heterofullerene $C_{59}N$ as a function of photon energy. The $C_{59}N$ molecule has an essentially identical structure to C_{60}, with the substitution of just one of the carbon atoms in the cage by a nitrogen atom. It is proposed that the observation of photoemission intensity oscillations essentially identical to those observed for C_{60} is a clear indication of the applicability of the photoelectron interference model.

The substrate used in this work was a *p*-type (B-doped) Si(111) wafer. A protective thermally grown oxide layer (15-nm thick) was removed prior to insertion into the vacuum chamber by HF etching followed by an oxidizing clean (H_2O_2:H_2SO_4, 1:1 for 10 min at 135 °C). The Si was
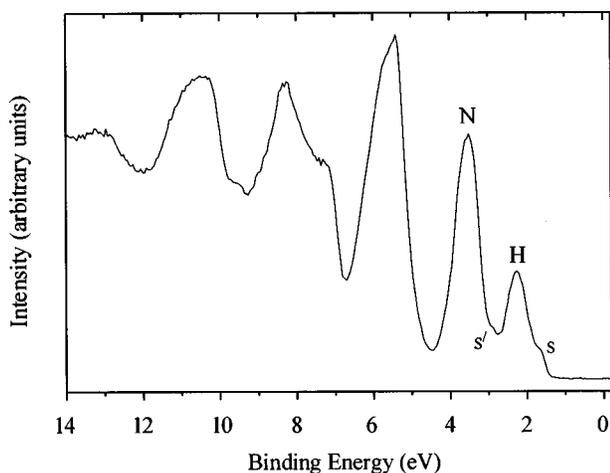
FIG. 1. The valence-band photoemission spectrum of the $C_{59}N$ film. The features indicated by **h** and **n**, respectively have predominantly $C2p\pi$ character and correspond to the HOMO and NHOMO of the C_{60} molecule. The HOMO of the nitrogen substituted material is apparent as the shoulder, **s**. This is thought to arise from the dimerization within the film to $(C_{59}N)_2$ and has considerable N character. The small feature **s'** is also thought to result from the presence of nitrogen in the molecule.

degassed and then flashed to 1000 °C in UHV to form the ordered (7×7) reconstruction of the clean surface. $C_{59}N$ was deposited by sublimation from a Ta crucible heated to 550 °C in a Knudsen cell. Prior to deposition, the source material was outgased and purified by running the *K* cell at increasingly high temperatures up to 550 °C. *Ex situ* atomic force microscopy (AFM) measurements indicated a deposition rate of 2.7 ± 0.7 ML min^{-1}. $C_{59}N$ was deposited for 5 h and 20 min in total, following which no trace of the Si $2p$ peak could be observed in the photoemission spectra at any of the photon energies employed. Valence-band photoemission spectra were measured on beamline 4.1 (Refs. 7 and 8) of the synchrotron radiation source at the Daresbury Laboratory in the UK. The spectrometer is housed in a single UHV chamber, equipped with a Scienta SES200 hemispherical electron energy analyzer with a radius of 200 mm and an angular acceptance of $\pm 5°$. Sample heating was effected by electron beam irradiation of the back of the sample. All of the spectra shown in the current work were recorded at normal emission and have been aligned to the Fermi edge of the Ta sample plate. The width of the Fermi distribution at room temperature was measured to be 0.2 ± 0.05 eV at $h\nu = 30$ eV.

Figure 1 shows the valence-band photoemission spectrum recorded from the $C_{59}N$ film using a photon energy of $h\nu = 30$ eV. The spectrum agrees well with that published for a thick-film (1000 Å) grown on an evaporated gold film substrate.[9,10] The majority of the spectral features are very similar to those of C_{60}. Peaks below about 9 eV binding energy are derived almost entirely from σ-bonding states. Between about 9 and 5 eV, a mixture of σ and π states contribute to the peaks, whilst above about 5 eV the peaks are almost entirely π-like in character. The strong peaks at 2.3 and 3.5 eV (labeled **h** and **n**, respectively in Fig. 1) are predominantly derived from C $2p$ interactions. These peaks essentially correspond to the highest occupied molecular orbital (HOMO) and next-highest occupied molecular orbital
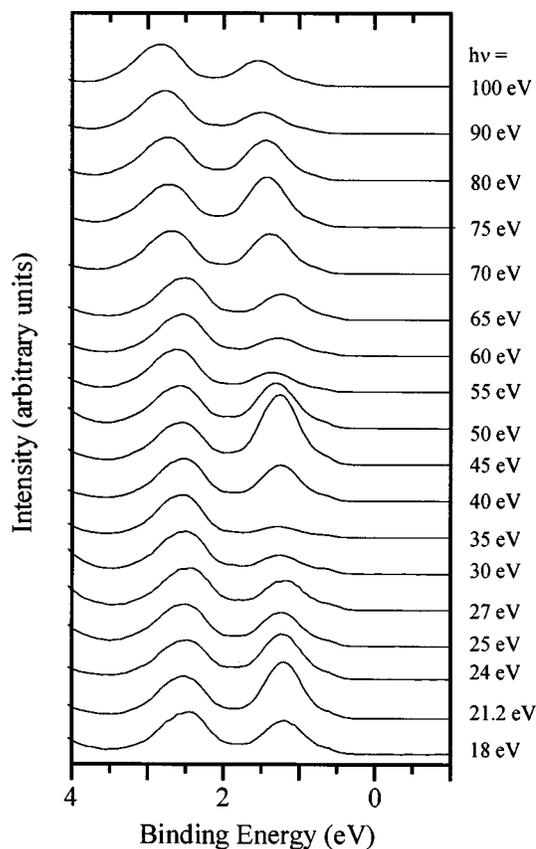
FIG. 2. Valence-band UPS spectra recorded at photon energies ranging from 18 to 100 eV. Spectra have been normalized to the intensity of the **n** peak at 3.5 eV. The quasiperiodic rise and fall in the intensity of **h** as the photon energy increases can clearly be seen.

(NHOMO) of the pure C_{60} molecule. The shoulder at the top of the valence band (**s**) and the weak feature at about 2.9 eV (**s'**) are not seen in the photoemission spectrum of C_{60}.

Very recent scanning tunnelling microscopy studies have shown that for low coverages, the $C_{59}N$ molecule adsorbs on Si(111) (7×7) as a monomeric species.[11] However, in previous work on thick films[10,11] similar to those used in these experiments, electron diffraction studies confirmed the existence of $(C_{59}N)_2$ dimers. Consequently, density-functional theory calculations of the density of states (DOS) used to explain the valence band photoemission spectroscopy explicitly assumed a dimerized structure. On the basis of the calculations, it was suggested that the shoulder at ~1.65 eV binding energy is related to the presence of the inter-$C_{59}N$ dimer bond. The HOMO for $(C_{59}N)_2$ is thus a molecular orbital that encompasses this bond. Calculations of the partial density of states showed that the electron density associated with this molecular orbital is located not only on the C atoms involved in the intercage bond, but also on the adjacent N atoms, resulting in a considerable degree of nitrogen character in the uppermost valence-band states.

Figure 2 illustrates the variations in the valence-band photoemission spectrum measured using photons with energies ranging between $h\nu = 18$ eV and $h\nu = 100$ eV. In this figure, the spectra have all been normalized to the maximum of the **n** peak at ~3.5 eV binding energy. The variation in the intensity of the **h** peak is clearly discernible. The normalized
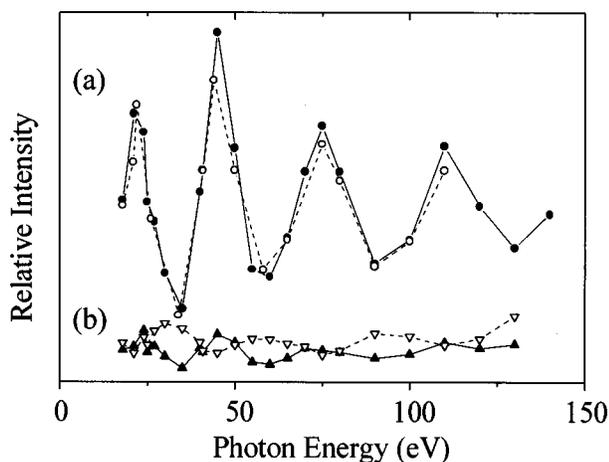
FIG. 3. (a) Filled circles show the variation in the intensity ratio I_h/I_n as a function of photon energy, where I_h and I_n are the intensities of peaks **h** and **n** measured for $C_{59}N$ from the spectra shown in Fig. 2. The open circles are the corresponding intensity ratios (I_{HOMO}/I_{NHOMO}) for C_{60}, measured from Fig. 2 of Ref. 6. (b) Variation in the intensity of the $C_{59}N$HOMO shoulder **s** with respect to peaks **h** (open triangles) and **n** (closed triangles) measured from the spectra shown in Fig. 2. Both sets of points are displayed on the same scale, but the points in (a) have been shifted up for clarity. The solid and broken lines are intended as guides to the eye.

intensity of this peak (i.e., the intensity ratio I_h/I_n) is plotted in Fig. 3(a) as a function of the photon energy of the exciting radiation. Also plotted in this figure are the corresponding normalized I_{HOMO}/I_{NHOMO} ratios measured from the spectra shown in Fig. 2 of Ref. 6, which shows similar oscillating behavior for C_{60}. The two plots are extraordinarily similar. Not only do the peaks in the relative photoemission intensity occur at the same energies, giving the same gradually increasing period to the oscillation, but the absolute values of the normalized intensities are also remarkably close.

Although the unoccupied states of $(C_{59}N)_2$ have been examined only for energies up to about 10 eV above the lowest unoccupied molecular orbital[10,11] (LUMO) the nitrogen substitution and molecular dimerization has a clear effect on the density of states. It is probable that the higher lying states will be affected in a similar manner. Although the effect on the empty states may appear minor, with the molecular orbitals retaining much of the C_{60} character, the width, degeneracy, and in certain cases even the position of the peaks in the empty-states spectra *are* altered from those of C_{60}. In the photoemission experiment this would certainly result in modified photoionization cross sections and changes in the period and amplitude of the oscillation in the measured peak intensities would be expected. The observation that the relative intensities of the two largest uppermost peaks in the spectrum are almost identical to those of C_{60} over the entire range of photon energies employed therefore strongly suggests that a model in which the photoionization cross-section is entirely dependent on the nature of the empty states involved in the photoemission process is incorrect. Conversely, it might be argued that interpretation of the intensity modulation in terms of the photoelectron interference model should not be possible for $(C_{59}N)_2$ since the molecule is no longer spherical. Nevertheless, it is clear that the photoelectrons responsible for the **h** and **n** peaks of Fig. 1 are mostly

emitted from carbon atoms that sit on the perimeter of two essentially spherical shells. Substitution of nitrogen for carbon in the $C_{59}N$ monomer has little effect on the shape of the molecule, with the bond lengths remaining similar to those of C_{60}.[12] On dimerization, charge is redistributed resulting ultimately in longer on-cage C-N and C-C bondlenghts in the vicinity of the dimer bond. Even so, since the cages are approximately spherical and of similar radius to C_{60}, they fulfill the prerequisites of the photoelectron interference model. It is, therefore, unsurprising that the observed oscillations should be so similar to those of the parent molecule.

Since it is unique to $(C_{59}N)_2$, examination of the shoulder (**s** in Fig. 1) that represents excitation of electrons out of the HOMO of the dimerized molecule ought to provide further information about the emission process. The absolute amplitude of this peak at all photon energies is expected to be considerably less than that of the **h** or **n** peaks due to the smaller density of occupied states. Moreover, the large degree of N $2p$ character means that the absolute peak intensity may be affected by the atomic subshell photoionization cross section, which shows some variation to the corresponding C $2p$ cross section, although this is relatively minor.[13] However, in neither model would the intensity of the peak be expected to oscillate with exactly the same period as either the **h** or **n** peaks.

Considering firstly the unoccupied molecular orbital approach. Regardless of the symmetry of the HOMO, it is located half an eV to lower binding energy of the **h** peak and has considerably greater nitrogen character. Even if the unoccupied molecular orbitals were identical to those of C_{60}, the degree of overlap between the initial and final states would be quite different and the photoionization cross section would maximize for different photon energies. On the other hand, considering the criteria necessary for interference of the photoelectron waves it is likely that under this model no oscillation in peak intensity would be expected at all. Density-functional theory calculations have shown the HOMO to be localized mainly on the nitrogen atoms and the intercage bond. Moving towards the opposite ends of the dimer, away from the central bond, the electron density on the C atoms in the cage is sharply reduced. The electron density therefore shows a marked gradation across each cage of the dimer and a certain amount is actually located outside of either $C_{59}N$ cage. *The* HOMO *cannot therefore be approximated by a spherical shell of similar radius to* C_{60}, *and no oscillation in the intensity of the resulting photoemission peak is expected.*

Unfortunately, analysis of the behavior of the HOMO peak with changing photon energy is not straightforward. The main difficulty arises when normalizing the spectra in order to measure the relative peak heights. Referring to the first study that reported the oscillatory behavior of the HOMO and NHOMO peaks of C_{60}, the peaks to higher binding energy also show intensity fluctuations with photon energy. This is seen most clearly in Fig. 2 of Ref. 1. In that work, the intensities of the HOMO and NHOMO peaks were normalized to the combined intensity of the peaks at around 8 eV binding energy. It was assumed that overall this feature should show no intensity modulation because of the mixed π and σ nature of the states involved. Constant initial state measurements later showed this to be an over

approximation.[2] That all of the peaks should show intensity oscillations as a function of photon energy is expected on the basis of the photoelectron interference model. In light of this observation, the intensity of the HOMO peak of $(C_{59}N)_2$ was considered relative to both the major low-binding energy features of the spectrum. The variation of the peak intensity is shown in Fig. 3(b) normalized to both the **h** and the **n** features of Fig. 1. The amplitude of the fluctuating curves obtained for either normalization of the HOMO peak is similar in both cases, the major difference being that the ''phase'' is reversed. This strongly suggests that the actual intensity of the HOMO shoulder is approximately constant throughout the photon energy range sampled. The oscillations that appear in the plot of relative intensities are then simply a result of the strong amplitude variation of the **h** and **n** peaks.

In conclusion, striking oscillations in the essentially C π derived features of the valence band UPS of a $C_{59}N$ film have been observed as a function of the photon energy employed. The relative intensities of the peaks and the spacings between maxima and minima are extremely similar to those recorded for the HOMO and LUMO of C_{60} over the entire photon-energy range examined. These observations clearly oppose a model, which depends on the exact nature of the initial and final states of the photoelectrons, but strongly support the photoelectron interference model of Hasegawa *et al.*[5,6] On the basis of this model, it is proposed that photoemission intensity oscillations should *not* be observed for the HOMO of $(C_{59}N)_2$. Although absolute measurements of the intensity of this peak were not possible, the observed relative intensities are not inconsistent with this suggestion.

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