Spectromicroscopy of \( \text{C}_{60} \) and azafullerene \( \text{C}_{59}\text{N} \): Identifying surface adsorbed water

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\( \text{C}_{60} \) fullerene crystals may serve as important catalysts for interstellar organic chemistry. To explore this possibility, the electronic structures of free-standing powders of \( \text{C}_{60} \) and \( \text{C}_{59}\text{N} \) azafullerenes are characterized using X-ray microscopy with near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy, closely coupled with density functional theory (DFT) calculations. This is supported with X-ray photoelectron spectroscopy (XPS) measurements and associated core-level shift DFT calculations. We compare the oxygen 1\( s \) spectra from oxygen impurities in \( \text{C}_{60} \) and \( \text{C}_{59}\text{N} \) and calculate a range of possible oxidized and hydroxylated structures and associated formation barriers. These results allow us to propose a model for the oxygen present in these samples, notably the importance of water surface adsorption and possible ice formation. Water adsorption on \( \text{C}_{60} \) crystal surfaces may prove important for astrobiological studies of interstellar amino acid formation.

Membrane production is considered to be one of the critical steps in the formation of amino acids in the interstellar medium, and ultimately to the earliest stages of life\(^1\). However, the molecular interactions between carbon, nitrogen and oxygen in space remain enigmatic. Recent studies from the Spitzer radio telescope\(^2\) have identified large amounts of crystalline \( \text{C}_{60} \) in interstellar outflows. Midinfrared bands at 7.0, 8.5, 17.4 and 19.0 \( \mu \text{m} \) match those for neutral \( \text{C}_{60} \)\(^3,4\), which has been suggested as a candidate for templating simple nucleobases in interstellar environments\(^5\). \( \text{C}_{60} \) crystal surfaces are a potential interstellar reaction membrane candidate; thus detailed characterization of the surface chemistry of fullerene crystal surfaces is required. However, quantitative analysis of spectroscopy data is complicated due to the potential ambiguity caused by carbonaceous impurities. For this reason it would be advantageous to also consider fullerene structures containing chemical markers, such as heterofullerenes.

Amongst heterofullerenes, the best-known and most studied species are the nitrogen-substituted azafullerenes, notably the mono aza\([60]\)fullerene (\( \text{C}_{59}\text{N} \))\(^6\)\(^\text{14}\), where a single carbon atom is replaced by nitrogen. The resultant carbon radical is stabilized by forming an intermolecular \( \text{sp}^3 \)-like bond with a similar radical carbon in a neighboring azafullerene, with a predicted binding energy on the order of 0.65 eV\(^15\). Thus the preferred structure at room temperature or below is the (\( \text{C}_{59}\text{N} \))\(_2\) dimer (Fig. 1)\(^16\). Little is known about the spontaneous oxidation behavior of azafullerenes as compared to \( \text{C}_{60} \)\(^17\), and even the nature and origin of \( \text{C}_{60} \) oxidation itself upon exposure to air remains controversial\(^\text{16,19}\).

Here we investigate the spectroscopic fingerprint of suspended clusters of \( \text{C}_{60} \) and (\( \text{C}_{59}\text{N} \))\(_2\) using near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS) combined with a range of density functional theory (DFT) modeling approaches.

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Previous near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy studies of fullerenes have relied on thin film samples deposited on surfaces. However, during fullerene film preparation, the thermal evaporation step can influence the formation as well as the interaction of the film with the substrate surface, especially in the case of azafullerenes. In addition, surface contamination can have a strong impact on NEXAFS spectra. For this reason, for the NEXAFS analysis, the azafullerene and fullerene powders were sonically dispersed in ethanol, and a drop of each solution was deposited onto lacey carbon films supported on copper transmission electron microscopy (TEM) grids. This allows us to study indirectly supported material located above holes in the lacey carbon film grid, avoiding the interaction of the measured sample region with the substrate.

We model the structures, possible oxidation products and pathways, and simulate spectra of pristine and oxidized fullerene and azafullerene species. Collectively these results allow us to establish a detailed picture of the morphology, electronic structure, and chemistry of these materials, notably including their interaction with water and other oxygen impurities.

Results and Discussion

NEXAFS Spectroscopy. Before considering the interaction between oxygen and fullerenes, we first properly characterize the carbon and nitrogen spectroscopic signatures of $C_{60}$ and $(C_{59}N)_2$.

The experimental and theoretical carbon 1$s$ spectra of $C_{60}$ and a projection of the theoretical spectrum onto $p$-components either orthogonal ($\pi^*$) or tangential ($\sigma^*$) to the $C_{60}$ cage surface are shown in Fig. 2. The spectrum is characterized by discrete peaks, and in general there is excellent agreement between theory and experiment, both for peak separations and intensities. Our experimental spectrum of $C_{60}$ is very similar to those reported previously in the literature. In order to account for electron-hole interactions we introduced a core-hole in the C 1$s$ orbital of the excited carbon atom. Figure 2 shows the effect of removing either 0 ("initial state"), 0.5 ("Slater transition state") or 1 ("final state") electron from this 1$s$ (C) core orbital (panels a–c, respectively). The best agreement comes from the half core-hole approximation (Fig. 2b), which is used in the rest of our study.
The spectral decomposition in Fig. 2d reveals that the peaks in the low energy range (284–289 eV) have C 1s excitation to final states of $\pi^*$ character, while the higher energy spectral features are due to C 1s excitation to final states of $\sigma^*$ character. Specific $\sigma^*$ peaks seen in the experimental spectrum from 290–296 eV stand out clearly in the theoretical spectrum decomposition. From this analysis, the first three peaks below 287 eV are assigned to C 1s excitations to the four degenerate $\pi^*$ molecular orbitals $t_{1u}, t_{1g}, t_{2u}$ and $a_g$, where the latter two are energetically very close. The last peak at 288.5 eV also corresponds to an $a_g$ orbital. We note that the small pre-peak seen in the modeling at around 283 eV is a screening artifact introduced by the half core-hole approximation as can be seen by its absence in the full core-hole data. Earlier GGA full core-hole modelling also gave good agreement to experiment, with some variation from our calculated spectra (see Supplementary Information), notably in peak spacings, probably due to differences in basis set construction (the previous study including reduced four-electron effective core potentials for all non-excited carbon atoms, and non-diffusive basis sets for minimization with added diffuse functions for the static exchange Hamiltonian).

We next turn to the C 1s spectrum of (C$_{59}$N)$_2$. The symmetry breaking from nitrogen substitution and fullerene dimerization means there are now 31 symmetrically inequivalent carbon sites, and it is necessary to calculate the spectrum for each of these (Fig. 3). There are 28 inequivalent carbon sites with a multiplicity of four and 3 with multiplicity of two (these lie on the central mirror plane marked in yellow). Of these three, site C1 corresponds to the sp$^3$ 4-fold coordinated atoms covalently linking the two fullerene cages together, which is clearly visible in its associated spectrum which lacks the $\pi^*$ related peaks from 284–288 eV.

If we now average these spectra using the appropriate weighting from their multiplicity, we obtain the averaged calculated spectrum, which is shown in Fig. 4 in comparison to the experimental C 1s spectrum of (C$_{59}$N)$_2$ measured by scanning transmission X-ray microscopy (STXM). Our experimental spectrum of (C$_{59}$N)$_2$ is very similar to those reported previously in the literature, with some variation from our calculated spectra (see Supplementary Information), notably in peak spacings, probably due to differences in basis set construction (the previous study including reduced four-electron effective core potentials for all non-excited carbon atoms, and non-diffusive basis sets for minimization with added diffuse functions for the static exchange Hamiltonian).

The nitrogen 1s spectrum of (C$_{59}$N)$_2$ is shown in Fig. 5. It exhibits a primary component centered at 401.5 eV and a larger, broader feature at 406 eV consistent with nitrogen neighboring sp$^3$-coordinated carbon. When compared to the N 1s spectrum of (C$_{59}$N)$_2$ reported by Schulte et al., there is considerable disagreement, in particular the separation of the two main peaks is different (4.8 eV in this work, 5.2 eV in ref. 14) and there is a major difference in the width and relative intensity of the first peak which can not be explained by instrumental differences. In particular the N 1s spectrum of (C$_{59}$N)$_2$ reported by Schulte et al. has a rather sharp peak at 401.5 eV (fwhm ~1 eV), whereas the corresponding feature on our spectrum is much broader (fwhm ~2 eV). We explored the possibility the signal in the Schulte et al. spectrum could be from trapped gaseous N$_2$. Subtraction of N$_2$ gas signal to remove this sharp peak does result in a much broader first peak, closer to that we have measured, but there is still a poor match to our result.
By contrast good agreement is found between our measured and calculated N 1s spectra, notably in the features in the extended σ* states and the low energy shoulder to the 401.5 eV peak. We note that our theoretical and experimental data correctly reproduces the key spectral features found in a recent simulated (C59N)2 NEXAFS N 1s spectrum31, including primary peak spacings and the presence of the small pre-peak shoulder. This gives us additional confidence in our results.

A key difference between the N 1s and C 1s spectra is that while the primary C 1s peak has strong π* character, the primary N 1s peak is mainly σ* in character. This is consistent with previous findings for EELS spectroscopy of nitrogen doping in single-walled carbon nanotubes 28. In the current study we can see however that some π* character is responsible for the low energy shoulder of this peak, due to slight deviation from full tetrahedral configuration imposed by the fullerene cage environment.

The spectroscopic influence of nitrogen substitution in the fullerene cage is twofold: first, the stronger core potential offered by the nitrogen atom manifests itself in a low-binding energy shoulder split-off from the highest occupied molecular orbital (HOMO), carrying significant nitrogen character32. This is, however, not to be associated with simple filling of the lowest unoccupied molecular orbital (LUMO) of the C60, as the excess electronic charge stays relatively localized on the nitrogen sites. The substitutional nitrogen atom in C59N is sp3-bonded, i.e. forms three σ bonds with its carbon neighbors, with its remaining two valence electrons forming a stable lone pair. This means the loss of a π bond in the associated hexagon-hexagon double bond, creating a neighboring carbon radical with an unpaired pz-electron. The carbon radicals of neighboring cages combine to form a σ bond between them. Thus, in terms of bonding, the conversion from C60 to (C59N)2 involves the elimination of only one π bond per fullerene, and some structural modification of nearby σ bonds around the substitutional and cross-linking sites (Supplementary Figure 3).

The heteroatom introduces changes to the electronic structure of the fullerene cage, observed as spectral broadening and the appearance of two structures in between the three highest valence band peaks in
photoemission\(^2\). As compared to the energy gap of \(C_{60}\) (\(~1.86\) eV), the energy gap between occupied and unoccupied states is smaller in \((C_{59}N)_2\) at 1.4 eV (ref. 22).

To summarise this section, we find good agreement between theory and experiment for the \(C 1s\) and \(N 1s\) spectra of \(C_{60}\) and \((C_{59}N)_2\). Small differences in peak positions and intensity are observed between these two species, caused by the relatively localised disruption to the fullerene bonding in the azafullerene dimer. While the first peak in the \(C 1s\) spectrum has \(\pi^*\) character, in the \(N 1s\) spectrum this peak has primarily \(\pi^*\) character with a small low energy \(\pi^*\) shoulder. It should be noted that the use of a statically screened electron-hole interaction via the Slater transition state allows accurate reproduction of the present NEXAFS data for both \(C_{60}\) and \(C_{59}N\). Additionally, such an approach means that for the carbon \(1s\) spectrum for \((C_{59}N)_2\), a weighted spectrum based on 31 half core-hole spectra for each inequivalent carbon site can be determined, allowing analysis of the contribution of each carbon atom to the resulting experimental spectrum. This demonstrates that while the static approach does not allow an explicit treatment of core-hole interactions, it is nonetheless a very powerful tool for the analysis of complex spectra.

### X-Ray Photoelectron Spectroscopy.

The discussion thus far has concerned the quantitative agreement between modeling and spectroscopy for \(C 1s\) and \(N 1s\) NEXAFS spectra. We next compare calculated \(C 1s\) and \(N 1s\) core level binding energies to those measured with XPS. An absolute energy comparison is essential to understand the interactions between molecules and (aza)fullerenes.

We find that although carbon atoms near the nitrogen site(s) do exhibit different calculated \(C 1s\) energies than those from pristine “bulk” \(C_{60}\), the binding energies are less than 40 meV higher already for next-nearest neighbors away from the N. Thus while the experimental \(C 1s\) spectrum is in theory a convolution of several peaks, within the experimental accuracy it is well described by the bulk value. For the dimer, we obtained \(N 1s–C 1s\) energy separations of 115.65 eV (\(\Delta SCF\)) and 115.73 eV (\(\Delta KS\)), in excellent agreement to our experimentally measured separation of 115.5 eV. This demonstrates the strength of this approach for the quantitative determination of relative core-level energies, with the \(\Delta SCF\) method featuring the additional benefit of having the same atomic reference energies for both the \(N 1s\) and \(C 1s\) calculations.

We note further that although it is not experimentally accessible due to dimerization, the calculated \(N 1s–C 1s\) energy separation for the single \(C_{59}N\) radical is 116.10 eV, implying that the interaction in the dimer lowers the \(N 1s\) level by about 0.4 eV (with the Kohn-Sham eigenvalues approximating the initial state energies showing a slightly larger difference of 0.7 eV). This is presumably due to slight differences in the chemical environment of the N atom and core-hole screening in the two systems.

### Calculated Interaction with Atomic Oxygen Species.

We next turn our attention to the nature of oxygen contamination in fullerene and azafullerene samples, which remains an open question in the literature. Both epoxide and annulene fullerene structures (Fig. 6a,b) have been successfully synthesized\(^33,34\). Density functional theory (DFT) studies of single oxygen addition to heterofullerenes found that \(C_{59}N\) and \(C_{59}HN\) showed similar epoxide formation and binding energies as \(C_{60}\) (ref. 17). However, it is not obvious how epoxides and annulenes would be produced via spontaneous \(O_2\) incorporation in \(C_{60}\) crystals upon air exposure. The most stable configuration for a single oxygen atom is cross-linking a fullerene dimer\(^35–38\) via a 2 + 2 cycloaddition reaction combining double bonds in neighboring \(C_{60}\) where the oxygen atom adopts an ether configuration in one of the cross-linked bonds (Fig. 6c). Dry air studies have suggested the presence of interstitial oxygen molecules sitting in the octahedral voids of the crystal\(^8\), and modeling has confirmed the octahedral sites as the most stable for \(O_2\) incorporation\(^38\).

The most stable configuration that we found for a single oxygen atom in \((C_{59}N)_2\) structures is the analogue of the bridging configuration of \(C_{60}\) dimers, i.e. an oxygen atom in an ether configuration in the cross-linking bond between \((C_{59}N)_2\) pairs in the dimer (Fig. 7a). As compared to \(C_{60}–O–C_{60}\) (Fig. 6c), replacing the \(sp^2\)-cross-linked carbon atoms with two non-bonded nitrogen atoms removes the second cross-linking bond between the fullerene cages and relaxes significant strain.

### Calculated Interaction with Water.

FTIR spectra have demonstrated the presence of both \(O_2\) and \(H_2O\) in \(C_{60}\) crystals exposed to air\(^39\), and testing \(C_{60}\) in air with varying humidity has suggested that the observed \(O 1s\) XPS signal was caused by \(H_2O\) exposure\(^40\). Indeed, \(C_{60}\) has a high affinity for water, as shown by its high free energy of hydration (\(\sim 90.5\) mJ/m\(^3\))\(^40\).

Before analyzing our experimental data, we first explore theoretically the feasibility of molecular \(H_2O\) interaction with fullerenes and azafullerenes. To the best of our knowledge, there is little modeling of the \(H_2O–C_{60}\) interaction. Tsetseris et al. showed that \(C_{60}–H(OH)\), i.e. \(H_2O\) dissociated to saturate a \(C_{60}\) double bond, is 0.1 eV less stable than \(H_2O\) in an octahedral void in the \(C_{60}\) crystal\(^38\), and models have been proposed of hydration cages forming around \(C_{60}\) when in solution\(^41–43\).

We calculate the binding energy of \(H_2O\) to isolated “gas-phase” \(C_{60}\) to be 0.34 eV, increasing to 0.56 eV when the \(H_2O\) molecule is placed in the octahedral interstitial void in fcc \(C_{60}\). The binding energy of \(H_2O\) to gas phase \((C_{59}N)_2\) is 0.32 eV, very similar to that for \(H_2O\) binding to \(C_{60}\). Since the nitrogen atoms are close to the cross-linked carbon atoms, they are spatially inaccessible to the \(H_2O\) molecule, which is forced to sit further away on the cage surface and does not interact strongly with the nitrogen. The result again reflects the earlier finding that the perturbation of the fullerene cage caused by nitrogen substitution remains localized around the nitrogen and its neighbors, with the rest of the cage closely resembling pristine \(C_{60}\).

Considering potential reactions of \((C_{59}N)_2\) with water, one possibility is that \(H_2O\) could saturate the C-C cross-linking bond between the cages, creating a \(C_{59}NH/C_{59}N(OH)\) pair. However, we found this structure to be 0.27 eV less stable than \((C_{59}N)_2\) with a neighboring \(H_2O\) molecule. Additionally, we calculate an extremely
high reaction barrier of 3.94 eV for this process, due to the difficulty in forcing the H₂O molecule between the two fullerene cages in close proximity. We hence conclude that water is likely to remain molecular in interstitial voids if present within the bulk azafullerene sample.

Considering now possible reactions involving H₂O and C₆₀, a new structural analogue to C₅₉N-O-C₅₉N can be proposed, namely C₆₀H-O-C₆₀H (Fig. 7c). This is 0.13 eV more stable than H₂O sitting in the interstitial space between two C₆₀ molecules (which we find isoenergetic with C₆₀ neighboring C₆₀H(OH) (Fig. 7d), close to the result of Tsetseris et al. 38). C₆₀H-O-C₆₀H thus represents the lowest total energy structure we obtained with a single H₂O molecule and C₆₀. However, entropic considerations will not favor this structure at finite temperatures, and similarly to the azafullerene case, there is a significant reaction barrier of 2.40 eV that needs to be overcome to form this structure from H₂O + 2C₆₀. It is possible such a process could be catalyzed, either by doping (in a -1 charge state this barrier drops to 1.66 eV with C₆₀H-O-C₆₀H now 0.24 eV more stable) or photocatalyzed (in the triplet state the calculated barrier drops to 1.67 eV).

Thus, even if catalyzed, the reaction barriers remain high enough that under conventional room temperature conditions we expect H₂O in the presence of C₆₀ crystals to remain in molecular form, as in azafullerenes.

Oxygen X-Ray Photoelectron Spectroscopy. We next turn to our experimental oxygen data and its interpretation. Figure 8 shows the O 1s XPS signal of our fullerene and azafullerene samples (with the C 1s found at 284.6 eV). While both samples show a high intensity component at 532.2 eV, the C₆₀ sample also shows another prominent oxygen component at 533.8 eV, only weakly present in the azafullerene sample despite the overall oxygen concentration being slightly higher there. In general, the oxygen concentration is comparable with previous studies 39. The elemental compositions of the samples are shown in Table 1.

The spatial resolution of STXM means we are able to collect NEXAFS spectra exclusively from single, indirectly supported crystalline regions. Notably we can compare our NEXAFS measurements, which are dominated by the bulk response of the crystallites, with the surface-dominated XPS data. In the individual C₆₀ crystallites we did not detect any O 1s signal with NEXAFS. The azafullerene sample, which is more porous and less crystalline, did show a weak O 1s NEXAFS signal; however, comparison with theoretical modeling suggests this is due to ethanol contamination (see Supplementary Materials), which was used as a dispersant for the NEXAFS sample preparation.

The STXM-NEXAFS result therefore suggests that the observed O 1s XPS signal does not come from the bulk of the fullerene and azafullerene materials. There are thus two possible explanations for the signal. The first is that it comes from amorphous regions present elsewhere in the sample. The second is that it comes from surface/sub-surface adsorbed species, to which XPS is particularly sensitive, but which would be masked by the NEXAFS signal of the bulk. It is important to note that there can be no XPS signal corresponding to ethanol, since solvent was not used to make the XPS samples.
In order to assign the two peaks at 532.2 and 533.8 eV identified by XPS, we calculated the \( \text{O} \) 1\( \text{s} \) energies for all the structures shown in Figs 6 and 7 using the \( \Delta \text{SCF} \) method (the \( \Delta \text{KS} \) method yielded slightly lower binding energies for both the \( \text{C} \) 1\( \text{s} \) and \( \text{O} \) 1\( \text{s} \) levels, but their separation was almost identical between the two methods in all cases), with the results given in Table 2. Considering first the experimental \( \text{O} \) 1\( \text{s} \) XPS peak at 532.2 eV, the energy given in Table 2 for the \( \text{OH} \) group in \( \text{C}_{60}\text{H(\text{OH})} \) is close to this value at 532.53 eV. However, the calculated \( \text{O} \) 1\( \text{s} \) binding energies of ether-bound oxygen in \( \text{C}_{59}\text{N-O-C}_{59}\text{N} \) and \( \text{C}_{60}\text{H-O-C}_{60}\text{H} \) are also very similar; hence, we cannot conclusively assign the measured energies to one specific bonding, but suggest it corresponds to either hydroxyl- or ether-bonded oxygen in the sample.

The second experimental peak at 533.8 eV has a higher binding energy than any of our calculated structures in Table 2, and indeed, such a high value is strongly indicative of water. Onoe et al. measured XPS for...
rather strongly bound given the ultra-high vacuum conditions used for XPS, which is corroborated by the large groups on both samples, with lower concentrations in the azafullerene sample. The water must necessarily be surface-sensitive, the XPS characterization identifies the presence of a surface water layer containing hydroxyl that NEXAFS identifies the presence of ethanol solvent within the azafullerene crystals. In contrast, as more single H2O molecule in the C60 FCC crystal pore. Thus the calculations are consistent with the assignment of this of H2O within the crystal, the bound H2O observed in XPS must necessarily be near the crystal surface (the estimated maximum escape depth of our photoelectrons is ~2–3 nm). The lower intensity of the 533.8 eV O 1s signal in the C59N sample, arising from water, is also consistent with its decreased crystallinity as compared to C60 (see Supplementary Materials).

To directly simulate the core level binding energy of bound water, we created a model of eight C60 molecules taken from the infinite FCC lattice containing the relevant pore, surrounded by 15 Å of vacuum on all sides. Then, we ran two core level calculations using the ΔKS method: one with a H2O molecule in the pore, and another with the H2O placed at the corner of the simulation cell, far from the fullerenes. Thus the contents of the cell were the same in both cases (483 atoms with a total of 1928 valence electrons), and any error in screening our method makes for molecules is likely of similar magnitude. We should note that these are the largest core hole calculations ever reported to the best of our knowledge.

After correcting the resulting O 1s values so that both C 1s levels again match the experimental value, we found adsorption of H2O into the pore to downshift its O 1s level by 1.0 eV. Although this is not quite as much as the 2 eV difference between our higher BE component (533.8 eV) and a reference value for gas-phase H2O (535.75 eV), it is of similar magnitude and in the correct direction. Additional calculations for a hydration shell of 80 H2O molecules around C60 gave nearly the same O 1s binding energy for H2O at the C59N surface as for the single H2O molecule in the C60 FCC crystal pore. Thus the calculations are consistent with the assignment of this peak to surface or sub-surface water.

The O 1s XPS results strongly resemble findings for surface bound water on metals, where two O 1s peaks in XPS are commonly observed (for a review see ref. 45), and assigned to H2O and hydroxyl groups in the surface water layer, respectively. The presence of bound hydroxyl groups enhances water binding. For example, two XPS peaks at 530.8 and 532.4 eV are observed for Cu(110) cleaned in UHV and then exposed to water at room temperature, similarly, water on Ru[0001] shows two O 1s XPS peaks at 531.0–530.8 eV and 532.7–532.3 eV (the precise position varies with coverage). There is also precedent for water layer formation on carbon nanomaterials; for example, bilayer water formation has been observed on the surface of graphene under UHV conditions. Thus our calculations, the XPS data, and comparison to the literature strongly supports the interpretation that our higher binding energy component is due to a surface water layer, resistant to evaporation even in the spectroscope vacuum, with the lower binding energy component due to hydroxyl groups present in this layer. We note as further evidence of the strong layer binding that when we applied an annealing step at 70 °C within the XPS chamber prior to measurement, the resultant O 1s signal remained unchanged.

In our case there was no deliberate introduction of water to the samples, which was rather adsorbed by the samples from the humid air of the laboratory over time. Daylight exposure in the laboratory can also help explain the presence of the strong hydroxyl signal, since it has been demonstrated that exposure of C60 to UV light in the presence of water leads to hydroxyl radical creation.

Discussion and Conclusions

Isolated suspended clusters of C60 and (C59N), were analyzed by a combination of nanoscale NEXAFS, XPS and various DFT approaches. Our study clearly shows the benefit of combining different complementary theoretical and experimental techniques in order to characterize such complex samples as completely as possible.

We show that the extra electron in the azafullerene is predominantly localized on the N atom, and interpret the primary low energy peaks in the C 1s as coming from carbon π* states, whereas the primary low energy peak in the N 1s are from σ* states. Interpretation of the observed oxygen signal is complicated, but we propose that NEXAFS identifies the presence of ethanol solvent within the azafullerene crystals. In contrast, as more surface-sensitive, the XPS characterization identifies the presence of a surface water layer containing hydroxyl groups on both samples, with lower concentrations in the azafullerene sample. The water must necessarily be rather strongly bound given the ultra-high vacuum conditions used for XPS, which is corroborated by the large

| Structure          | Calculated O 1s [correction] (eV) |
|--------------------|----------------------------------|
| C60-O-C60H         | 532.56 [+0.39]                   |
| C60-O-C60          | 532.69 [+0.39]                   |
| C59N-O- (annulene) | 533.43 [+0.39]                   |
| C59N-O > O         | 533.00 [+0.39]                   |
| C60H(OH)           | 532.53 [+0.39]                   |
| C59N(OH)           | 533.01 [+0.26]                   |
| C60N-O-C59N        | 532.49 [+0.26]                   |

Table 2. Calculated O 1s core-level binding energies for the different structures in Figs 6 and 7. The energies are shifted so that the C 1s energy of the corresponding unmodified structure (C60 or (C59N)2) matches the experimental value of 284.6 eV, with the applied corrections given in brackets.
O 1s downshift of around 2 eV as compared to gas-phase water. This wetting behaviour strongly resembles that observed on many metal surfaces.

The presence of high levels of surface/subsurface adsorbed water in fullerene crystals, even under ultra-high vacuum conditions, has many important implications. One in particular is in the field of astrochemistry and astrobiology. Recent studies from the Spitzer radio telescope have identified large amounts of crystalline C_{60} in interstellar outflows. We propose here that the C_{60} crystal surfaces may serve as substrates facilitating the formation of amino acids in the interstellar medium, and ultimately the earliest stages of life.

If water is strongly surface bound to C_{60}, we could speculate that this may also be the case for other gaseous species. Surface reactions with water could then be catalyzed by kinetic confinement on the two-dimensional C_{60} crystal surface, with further mechanical confinement brought about by the surface rugosity. Surface reactions could be additionally catalyzed by UV-adsorption and energy transfer from the underlying fullerene crystal. C_{60} is known to be a highly efficient UV-absorber that promotes radical formation, for example converting triplet O_{2} to the singlet state with very high quantum yield, and can in the presence of water and UV generate hydroxyl radicals. Thus C_{60} crystals would be able to absorb the large amounts of available high energy UV-light present in and around such interstellar outflows, and direct it towards catalyzing surface reactions.

**Methods**

C_{60} was purchased from Bucky USA (99.5% grade), stored in the lab for several months and used as received. The details of azafullerene (C_{60}N_{2}) synthesis have been reported elsewhere. Briefly, starting from C_{60}, [60]-N-MEM ketolactam is isolated following a two-step procedure. A degassed solution of the ketolactam in o-dichlorobenzene is refluxed under argon for 15 min with an excess of p-toluenesulfonic acid. After the reaction mixture is cooled, flash column chromatography using silica gel with toluene as eluent afforded azafullerene (C_{60}N_{2}), as the least polar fraction. The material was further purified by high-performance liquid chromatography (Buckyprep column 20 x 250 mm, toluene eluent, 20 mL/min flow rate, 333 nm UV detection). The final HPLC track shows only a single peak after recycling, the profile indicating the purity is >99.99%. The azafullerene products after purification by HPLC, were stored in flat clear vials (4 mL/14.75 x 45 mm), with screw neck and with clear screw cap closed top Teflon, 1.5 mm (purchased from MACHEREY-NAGEL GmbH & Co. KG) at 25 °C and humidity 20%. They were prepared and transported between synthesis and characterization laboratories over a period of a few months. Storage in characterization laboratories was far from other chemical products.

STXM spectromicroscopy was used to analyze selected regions of the sample, taking advantage of its nanoscale spatial resolution. The carbon 1s spectra were recorded using the ambient STXM on the 10ID-1 soft X-ray spectromicroscopy (SM) beamline at the Canadian Light Source (CLS) in Saskatoon, Canada. This beamline has an energy resolving power E/ΔE > 5000. In STXM monochromatic X-rays of different energies are focused onto the sample by a Fresnel zone plate and the transmitted X-rays detected. The spectra were obtained by raster-scanning the sample at the focus of the X-rays over a range of photon energies so that a sequence of images at different energies was acquired, known as a “stack.” The nitrogen 1s spectra were recorded on a different region of the same sample with the STXM on beamline 5.3.2.2 at the Advanced Light Source in Berkeley, USA. Data processing was similar in both cases. The oxygen 1s spectra were measured with the full field transmission X-ray microscope (TXM) at the U41-FSGM beamline, BESSY II electron storage ring, Berlin, Germany. The spectra were recorded at room temperature in transmission mode by taking a sequence of images over a range of photon energies covering the investigated adsorption edges with a spectral resolution larger than 5000. The zone plate used provided a spatial resolution of 25 nm. Stack alignment, conversion to optical density, and extraction of NEXAFS spectra from small, free-standing regions were performed using the aXis2000 software. Since the photon flux at the sample varies as a function of energy and time, the aligned image sequences were converted to optical densities by dividing the transmitted signal recorded on the sample region by the incident photon flux recorded at a sample-free region. Thus, the ultimately acquired image sequences at different energies provide spatially resolved NEXAFS spectra.

X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Escalab 220XI XL with background pressure of 1 x 10^{-10} Torr, equipped with a source of monochromatic Al Kα X-rays (hν = 1486 eV). The escape depth of the photoelectrons is typically 2–3 nm, and the energy resolution was 0.6 eV. An electron gun (-1 eV) was used to compensate built-up charge on the specimen surface during the measurements. The samples for XPS measurements were prepared by pressing the specimen into a pellet, avoiding the need for a solvent. A conductive double-face tape was used to attach the pellet to a sample holder.

Density functional theory calculations of different fullerene and azafullerene structures, their complexes with oxygen and water, and associated formation barriers were performed using the LDA-PW91 exchange-correlation functional as implemented in the AIMPPro code. Spin-polarized calculations were carried out using supercells, fitting the charge density to plane waves with an energy cutoff of 150 Hartrees. Relativistic pseudopotentials generated by Hartwigsen, Goedecker and Hutter were used. 28, 40 and 40 independent Gaussian functions were used as basis sets for carbon, nitrogen and oxygen respectively. Periodic boundary conditions were applied, with supercell sizes checked and chosen to be sufficiently large (vacuum distance between all structures being larger than 13 Å) to avoid interactions between fullerenes in neighboring cells. Electronic level occupation was obtained using a Fermi occupation function with kT = 0.04 eV. Absolute energies were converged in the self-consistency cycle to better than 10^{-8} Ha. Atomic positions were geometrically optimized until the maximum atomic position change in a given iteration dropped below 10^{-5} Bohr radii. Diffusion barriers were calculated using the climbing nudged elastic band method, with typically 20 images between the initial and final structure.

Simulated X-ray adsorption spectra were calculated using the WIEN2k program package with the LDA functional and using the GGA-PBE optimised atomic structures. The GGA functional is better suited for the geometry optimisation, whilst our test calculations demonstrated that LDA gave slightly better C 1s peak separations for C_{60} than GGA for NEXAFS simulations (see Supporting Materials). In order to describe properly the impact of the two-particle electron-hole interactions on the XAS spectra, one should go beyond DFT by using
the Bethe-Salpeter approach\textsuperscript{65} or time-dependent DFT\textsuperscript{66}. Here, due to the size of the systems, we have chosen to mimic these many-body effects by considering a static screened electron-hole interaction using the Slater transition state, i.e. a half-reduced occupation in the C 1 s and N 1 s core levels when calculating the the C and N 1 s NEXAFS of C\textsubscript{60} and (C\textsubscript{59}N)\textsubscript{2}. A half-electron uniform background was added to perform these calculations. The broadening of our theoretical spectra was done in two steps by first considering a Lorentzian to account for the core-hole lifetime using tabulated values\textsuperscript{67}, and adding an energy-dependent broadening to account for the excited state lifetimes\textsuperscript{68}. For the energy-dependent broadening we considered a plasmon frequency of 8 eV for both C 1 s and N 1 s spectra. In order to compare our theoretical spectra with experiment, an energy shift which depends on the system and level of theory is needed. For the three C 1 s spectra of C\textsubscript{60} using 0, 0.5 and 1 core-holes, energy shifts of 282.7, 283.0 and 283.3 eV were used, respectively. For (C\textsubscript{59}N)\textsubscript{2} energy shifts of 284.0 and 399.5 eV were used for the N 1 s and C 1 s spectra, respectively.

For calculations of the C, N and O 1 s core-level binding energies, we utilized two methods based on density functional theory total energy differences, as implemented in the grid-based projector-augmented waves (PAW) simulation package GPAW\textsuperscript{66\textsuperscript{5}70}; a standard delta Kohn–Sham (\(\Delta KS\)) calculation with a projector-augmented wave dataset including an explicit core-hole on an atom of interest\textsuperscript{44}, and a novel all-electron extension of the delta self-consistent field (\(\Delta SCF\)) method\textsuperscript{72}. In the latter, the core electrons are included in the valence, enabling an explicit all-electron calculation within the PAW scheme\textsuperscript{73}. Exchange and correlation for these calculations were estimated by the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation\textsuperscript{45}, yielding significantly more accurate core level binding energies than the LDA\textsuperscript{72}. In each case, we calculated via total energy differences the respective 1 s energy and compared this to the C 1 s energy for a carbon atom far away from the N site(s).

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Author Contributions

C.B. initiated the project, N.T. and G.R. synthesized the \((\text{C}_{59}\text{N})_2\) samples. C.B., A.P.H., M.S. and X.Z. performed the CLS experiments and associated data analysis. A.P.H. and X.Z. performed the ALS experiments and analysis. C.B. and P.G. performed the BESSY II experiments. C.B. and M.S. performed the XPS studies. X.R. and P.B. performed the NEXAFS simulations. T.S. performed the XPS core-level shift calculations. D.E. and C.P.E. performed the structural DFT calculations and proposed the structural and astrochemical models. D.E., C.P.E., X.R., T.S., C.B. and M.S. analyzed the data and wrote the paper. All authors contributed corrections and modifications.

Additional Information

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