Electron energy loss spectra of C_{60} and C_{70} fullerenes


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Abstract

The electron energy loss spectra of C_{60} and C_{70} fullerenes are investigated using spectroscopy measurements and theoretical calculations. An additional peak has been identified for C_{70} above the carbon K-edge onset from our high-resolution electron energy loss spectra and analysed by density functional theory. Good agreement between theory and experiment is obtained, and the additional peak is found to be due to the electronic states associated with the 10 equatorial atoms in C_{70}.

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1. Introduction

After the discovery of the truncated icosahedral structure of C_{60} [1], the name ‘fullerene’ denoted a new form of spheroidal carbon nanostructures. Shortly afterwards, an extraordinary form of nearly one dimensional tubular structure, the carbon nanotube, was identified as a by-product of the fullerene synthesis [2]. Since this discovery and the successful large scale production of fullerenes [3], fullerenes and nanotubes have been investigated extensively for their structural and chemical properties [4]. Their nano-scale size and electronic properties can be used for molecular devices [5], and their hollowness can be used to store atoms or small molecules [6,7]. Furthermore, the significant modulation of electronic and magnetic structure by adsorption of additional atoms [7] opens the possibility of potential applications to molecular sensors [8] and to solid-state quantum computation [9].

A fullerene consists of twelve pentagonal rings, and a suitable number of hexagonal rings and all pentagonal rings are surrounded by hexagonal rings, obeying the so-called isolated pentagon rule (IPR). The IPR is based on the finding that fullerenes with isolated pentagonal rings are kinetically more stable than those with conjugated pentagonal rings due to the high chemical reactivity and strain of the fused pentagonal rings [10]. Buckminsterfullerene, C_{60}, has I_{h} point group symmetry and all 60 atoms are equivalent, while C_{70} has D_{5h} symmetry with five inequivalent atoms [4]. These two are the most abundant fullerenes and their physical and chemical properties have been studied with various experimental methods [11–16] and many different levels of theoretical calculations [4,17–22]. It is worth noting that density functional theory (DFT) calculations have demonstrated reasonable agreement with experimental observations for structural [18–21], vibrational [20], and electronic properties [18,19], even within the local density approximations (LDAs). Although the band gap is underestimated [22], the energy level spacing among filled states showed good agreement with experimental data [18]. Better agreement in structural properties was reported by more precise calculations using gradient corrections [23].

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In this report, we study the electronic structure of C_{60} and C_{70} using electron energy loss spectroscopy (EELS) and DFT calculations. Compared to C_{60}, an additional peak for C_{70} is observed in high-resolution EELS data and the origin of it is identified by our DFT calculations.

2. Experimental

The samples used in this study were prepared using a precipitation method. This involved 99.5% pure powder (Sigma–Aldrich Ltd.) was dissolved in carbon disulfide and then mixing with an excess of methanol to precipitate fullerene crystals. The nanocrystals produced in this manner vary in shape and size [24]. The carbon K-edge in EELS of C_{60} and C_{70} was measured using a monochromated FEI Tecnai 200 kV transmission electron microscope operated at 120 kV with a zero loss peak full-width half-maximum of 0.14–0.20 eV. The background was subtracted from all spectra. Spectra were all acquired at 120 kV in order to reduce electron beam damage occurring during the long acquisition times necessary to record the data. The spectra represent the transition from the carbon 1s core level to the final states having mainly p-like orbitals [25].

3. Computational

The theoretical calculations were performed using DFT within LDA and generalised gradient approximation (GGA) as implemented in DMol³ code [26]. The exchange-correlation functionals used are Perdew–Wang for LDA [27] and Becke–Lee–Yang–Parr (BLYP) for GGA [28,29]. All electron Kohn–Sham wave functions are expanded in a local atomic orbital basis set with each basis function defined numerically on an atomic centered spherical mesh. A double numeric polarised basis set is used. Geometries are optimised until the maximum force on each atom is less than 10^{-4} eV/Å and the total energy change is less than 5 \times 10^{-5} eV.

4. Results and discussion

C_{60} has very high symmetry (I_h) with six fivefold, 10 threefold, 15 twofold symmetric axes, and inversion symmetry. Twelve pentagons are surrounded by 20 hexagons and vice versa, so that there are two kinds of bonds: the bond between the pentagon–hexagon ring (p–h bond) and that between the hexagon–hexagon ring (h–h bond). Fig. 1a shows the optimised geometry from two different viewpoints in a ball-and-stick form. The C_5 symmetric axis is normal to the plane in the left column while it is horizontal in the right column. The p–h and h–h bond lengths differ by about 4% and are calculated to be 1.440 and 1.389 Å (LDA) and 1.457 and 1.405 Å (GGA-BLYP), respectively. Comparing to the experimental values of 1.458 Å (p–h bond) and 1.401 Å (h–h bond) [30], GGA-BLYP functional shows better agreement than LDA. Bond lengths calculated by various methods and experimental values are listed in Table 1. For comparison, the experimental carbon-carbon bond lengths are 1.54 Å (diamond), 1.42 Å (graphite, in plane), and 1.34 Å (typical double bond) [32]. The shorter length of h–h bond indicates that the π orbitals are not delocalised evenly over all the fullerene bonds as in graphite. The h–h bond will show stronger chemical reactivity than the p–h bond. For example, the h–h bridging ring between two C_{60} molecules in a dimer is 0.8 eV/dimer lower in energy than for p–h bridging rings [33]. The calculated bond orders are 1.15 (p–h bond) and 1.34 (h–h bond).

The structure of C_{70} is more complicated than C_{60}. The 10 additional atoms at the equator generate five additional hexagonal rings and lower the symmetry of the fullerene to D_{5h}, resulting in five inequivalent atoms and eight different bonds. The optimised geometry is shown in Fig. 1b with five inequivalent atoms labeled. The calculated bond orders are in the range from 1.16 to 1.33, similar to those of C_{60}. One can see that the bond lengths near the poles are similar to those of

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1 Note that previous studies [13–16] have synthesised and measured fullerene films rather than nanocrystals.

2 BLYP functional showed the best agreement to experimental data of structural properties among GGA functionals [23].
C\textsubscript{60}, since the local structure is the same, and the longest bonds are found at the equator. Again, we find the best agreement to experimental values is given by the GGA-BLYP functional, as listed in Table 1. We have, therefore, used GGA-BLYP results for further analysis.

The eigenspectra of the C\textsubscript{60} and C\textsubscript{70} fullerenes are depicted in Fig. 2. The height of the lines is proportional to the number of states, and the lowest unoccupied molecular orbital (LUMO) is set as the zero of energy. The energy gap between the highest occupied orbital (HOMO) and LUMO is 1.658 and 1.714 eV for C\textsubscript{60} and C\textsubscript{70}, respectively. The C\textsubscript{70} spectrum has lower degeneracy compared to that of C\textsubscript{60} due to the lower symmetry: for C\textsubscript{60}, the $\text{Ih}$ symmetry group can be decomposed into $a$, $t_1$, $t_2$, $g$, and $h$ with 1, 3, 3, 4, and 5 dimensionality, respectively, and the inversion symmetry makes pairs of each representation, labeled as $g$ (symmetric) and $u$ (antisymmetric). For C\textsubscript{70}, the subgroup of $D_5\text{h}$ ($a_1, a_2, e_1,$ and $e_2$) has lower dimensionality (1, 1, 2, and 2). Both the LUMO and second LUMO of C\textsubscript{60} are triply degenerate ($t_1u$ and $t_1g$, respectively) while those of C\textsubscript{70} are not degenerate ($a''_1$ and $a'_1$, respectively) [4].

The experimental high-resolution EELS data and the calculated density of states (DOS) of C\textsubscript{60} and C\textsubscript{70} fullerenes are depicted in Fig. 3. Note that the significant difference between C\textsubscript{60} and C\textsubscript{70} EELS data is a peak at about 0.70 eV in the case of C\textsubscript{70}, which is not found in C\textsubscript{60}. The high-resolution EELS data enable us to detect the difference between C\textsubscript{60} and C\textsubscript{70}, as previously reported by Terminello et al. [13]. More details on our comparative study with low and high-resolution EELS data can be found elsewhere [24]. To simulate the experimental spectra, we used a variable broadening width of $0.14 + 0.14 \times |E - E_{\text{LUMO}}|$ eV, where the first term corresponds to the experimental resolution of 0.14 eV and the second term represents the excited state lifetime effect. The projected DOS of p-orbitals are used for comparison since the EELS data we are investigating is associated with mainly p-like orbitals.

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Table 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>Number of bonds</th>
<th>C\textsubscript{60}</th>
<th>C\textsubscript{70}</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-h</td>
<td>60</td>
<td>1.440</td>
<td>1.439</td>
</tr>
<tr>
<td>h-h</td>
<td>30</td>
<td>1.389</td>
<td>1.387</td>
</tr>
<tr>
<td>LDA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA [23]</td>
<td></td>
<td>1.438</td>
<td>1.383</td>
</tr>
<tr>
<td>GGA-BLYP</td>
<td></td>
<td>1.459</td>
<td>1.431</td>
</tr>
</tbody>
</table>

Bond lengths are in Å. The corresponding sites are labeled in Fig. 1.

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The coefficient in the second term is purely empirical value: 0.04 was used in [21] and 0.2 was used in [18].
We do not expect a perfect match between EELS and projected DOS data because: (i) the EELS data are taken from nanocrystalline fullerene samples whereas the projected DOS have been calculated for fullerene molecules, (ii) the calculated unoccupied eigenvalues of the Kohn–Sham equation are not true excitation energies and are thus not guaranteed to produce an accurate description of the quasiparticle energies with the excitation of 1s core electron, and (iii) we have neglected non-dipole contributions to the transition probability. Fullerenes are sensitive to the electron beam so that damage of the sample cannot be ruled out, although efforts were made to reduce beam damage as much as possible. Nevertheless, we see from Fig. 3 that the projected DOS of C\textsubscript{70} shows a peak at about 0.7 eV, where the additional peak in the EELS data is found experimentally. Detailed analysis of this peak is given later.

For C\textsubscript{60}, two peaks in the projected DOS are found, one at 1.02 eV (\(t_{1g}\)) and a larger peak at 2.05 eV (\(t_{2u}\) and \(h_{g}\)) above the LUMO, similar to previous DFT results [19]: solid C\textsubscript{60} was found to have two distinct peaks at about 1 eV (\(t_{1g}\)) and 2 eV (\(t_{2u}\) and \(h_{g}\)) with band dispersion of about 0.4 eV [19] within LDA calculations. One can notice that our EELS data from nanocrystalline C\textsubscript{60} in Fig. 3a differ from those reported for C\textsubscript{60} films [13–16]. In the spectra from films, peaks at about 1 eV (\(t_{1g}\)) and 2 eV (\(t_{2u}\) and \(h_{g}\)) with band dispersion of about 0.4 eV [19] within LDA calculations.

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5 The core–hole effect [35] is not taken into account in this study.

6 Large band dispersion of \(\geqslant 0.7\) eV was reported by GW approximations [22].
two peaks are found at about 1 and 2 eV above the edge onset [13–16], which appears as one broad peak at 1.65 eV in our spectrum. This could be due to the different sample preparation methods as described in Section 2.

In order to identify the origin of the additional peak at about 0.7 eV found in high-resolution EELS measurements, the local DOS of each symmetry-unique site, a, b, c, d, and e, in C70 is calculated and depicted in Fig. 4a. The same variable width of 0.14 + 0.14×|E – E_LUMO| eV is used for all the local DOS and total DOS and the height of the lines amongst the delta functions represents the degeneracy of each state. From the total DOS at the bottom of Fig. 4a, one can see that the peak at about 0.70 eV originates from the two energy states at 0.494 and 0.738 eV, which are marked by arrows. The local DOS of each site clearly shows that the lower state (0.494 eV) originates from the equatorial atoms (site e) and their first nearest neighbours (site d), whereas the higher state (0.738 eV) originates from the rest of the C70 sites (a, b, and c). This is different from the C60 fullerene, where the molecular charge for any energy state is evenly distributed over all 60 atoms. The excited-state density plots of C70 corresponding to these two energy states are shown in Fig. 4b, and they confirm the significant contribution of the equatorial atoms to the lower state at 0.494 eV (left) and that of polar atoms to the higher state at 0.738 eV (right). This analysis explains the difference in the EELS between C60 and C70 as originating from the difference in the electronic states due to the 10 additional equatorial atoms in C70.

5. Conclusion

Using DFT calculations and high-resolution EELS measurements, the electronic structure of C60 and C70 fullerenes are systematically studied. The 10 additional atoms at the equator in the C70 fullerenes induce structural changes and lower the symmetry from that of C60. Comparing the local DOS to EELS data, we identify the additional peak in the EELS data of C70 as due to the electronic states associated with the 10 additional equatorial atoms.

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