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How the bond length can affect C₇₀ DOS and EEL spectra

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Abstract. The combination of electron energy loss (EEL) spectroscopy and density functional theory can lead to an understanding of how changes within a material lead to changes in electronic structure. In the past, C₇₀ EEL spectra have been interpreted using molecular and crystalline calculations. Although the shape of EEL spectra was explained well in both cases, the molecular calculation attributed the second peak in the spectrum to the ten equatorial atoms, which was not found to be the case in the crystalline calculations. In this paper we have studied the effect of variations in bond length on the density of states, and use this to explain the differences between the two previous calculations.

1. Introduction

In electron energy loss (EEL) spectroscopy, core electrons are excited into the empty states above the Fermi level. This provides an experimental probe of the unoccupied density of states (DOS) of a material. Density functional theory (DFT) can be used to calculate the DOS of different model structures. This allows models to be constructed in order to probe the effect of changes in the structure on both the DOS and EEL spectrum. In the case of materials such as fullerenes, this combination of EEL spectroscopy and DFT can lead to an understanding of how changes in the molecule result in changes in the electronic structure. This understanding is important for increasing the range of potential applications for these molecules.

Experimental EEL spectra have been collected by several authors from C₇₀ thin films [1] and nanocrystals [2]. Comparison of the C₇₀ spectrum and the unoccupied DOS of a C₇₀ molecule has allowed the second peak in the EEL spectrum to be associated with the ten equatorial carbon atoms in the C₇₀ molecule [3]. These atoms are highlighted as ring e on the C₇₀ molecule shown in Figure 1a. Simulations of EEL spectra from a C₇₀ crystal, however, showed that this peak cannot be associated only with the equatorial atoms [4]. In this paper we show the results of a study of the effects of the bond lengths in the C₇₀ molecule on the DOS, and provide a possible explanation for the different interpretations of the second peak in the molecule and crystal results.

2. Model structures

The C₇₀ molecule used by Lee *et al.* [3] to calculate the unoccupied DOS was optimized using the DFT code DMol³ so that the maximum force on each atom was less than 10⁻⁴ eV/Å and the total energy change was less than 5x10⁻⁵ eV. There are five inequivalent atoms in the molecule and eight different bond lengths ranging from 1.398 to 1.477 Å. The unoccupied DOS was calculated using a generalized gradient approximation (GGA) functional with the DMol³ code.

The C_{70} crystal used for the EEL spectra simulations [4] was that determined experimentally by van Smaalen *et al.* [5] for the low-temperature phase of C_{70} . A model of the unit cell is shown in Figure 1b. It is an orthorhombic unit cell, with 40 inequivalent atoms and space group $Pnma$. The bond lengths vary from 1.37 to 1.46 Å. The calculation of the EEL spectra was carried out with the all-electron DFT code WIEN2k [6] using the local density approximation (LDA) functional and was performed for a polycrystalline sample and a beam energy of 120 keV.

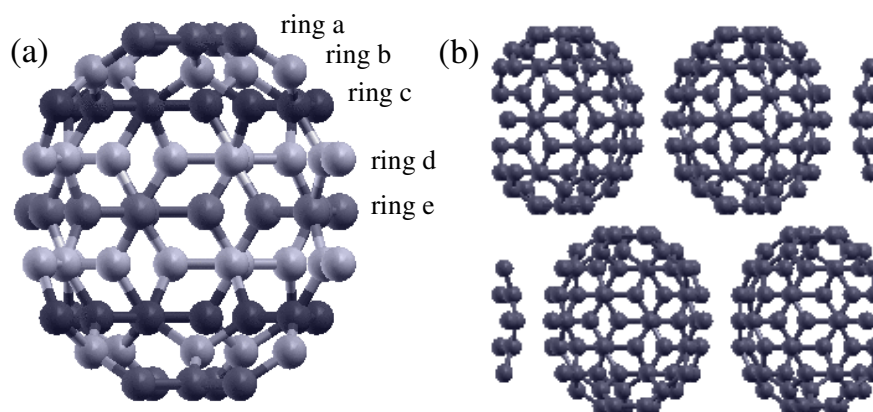


Figure 1: C_{70} molecule showing the different rings of inequivalent atoms (a) and the C_{70} crystal structure determined experimentally by van Smaalen *et al.* [5] and used previously to calculate EEL spectra [4] (b).

3. Calculations

Optimisation of the C_{70} crystal structure used for the previous EEL simulations was carried out using VASP, the Vienna Ab-initio Simulation Package [7]. The optimisation was performed using a GGA ultrasoft pseudopotential with a single k-point allowing changes in only in the ion positions and not in the unit cell shape or volume. The forces were reduced to less than 0.03 eV/Å.

Once the cell had been optimised, the number of k-points was increased so that the DOS could be calculated. A 2x2x3 mesh, with 8 irreducible k-points, was used to calculate the DOS for both the optimised and un-optimised structures.

4. Results

In order to be able to compare the VASP DOS calculations with the previous WIEN2k EEL spectra simulations, we first compare the DOS for the un-optimised structure calculated using the WIEN2k and VASP codes. Figure 2 shows the total DOS calculated by the two codes and, as can be seen from the figure, there is good agreement between the two. The DOS have been aligned using the Fermi level, and the HOMO has been set to zero.

During the optimisation, the ion positions were allowed to move. The optimised structure retained the symmetry of the original structure and the only differences between the optimised and un-optimised structures are the bond lengths, which range from 1.39 to 1.46 Å in the optimised case and from 1.37 to 1.46 Å in the un-optimised case. Figure 3 shows the total DOS for the un-optimised and optimised structures. The two graphs have been aligned using the LUMO. As can be seen from the figure, the changes in the bond length as a result of the optimisation have caused changes in the DOS. In particular, the unoccupied DOS within the first eV above the LUMO has changed significantly. This is the area of the DOS which is related to the first two peaks in the EEL spectra. One of the notable differences is the presence of the peak at ~0.7 eV in the optimised spectrum. This difference is investigated by splitting up the total DOS into the contributions from the rings shown in Figure 1. (Note that in a crystal, atoms within one ring are no longer equivalent.)

Figure 4a shows the contribution to the DOS from an atom in each of the five rings in the optimised structure. There are two peaks in the DOS at about 0.7 and 1.0 eV above the Fermi level which can be related to the two states at 0.50 and 0.74 eV above the LUMO in the molecular case which is shown in Figure 4b. The peaks are not at the same absolute energy values due to the broadening of the molecular energy states in the crystalline structure. Figure 4b also shows the isosurfaces of the two states. The distribution of density across the molecule agrees very well with the DOS from the optimised crystalline structure. In particular, the main contributor to the lower of the two states is ring e, the equatorial atoms.

Figure 5 show the DOS of those same atoms in the un-optimised structure. From comparison of figures 4a and 5, it is possible to see that the peak at ~0.7 eV in the optimised structure has moved downwards towards the Fermi level in the un-optimised structure. In the un-optimised case, it would be considered as contributing to the first peak in the EEL spectrum, and in the optimised case, it would be considered as contributing to the second peak. This is a subtle difference, and both previous calculations explained well the experimental data: it does, however, account for the differences in the interpretation of the second peak in the two previous calculations.

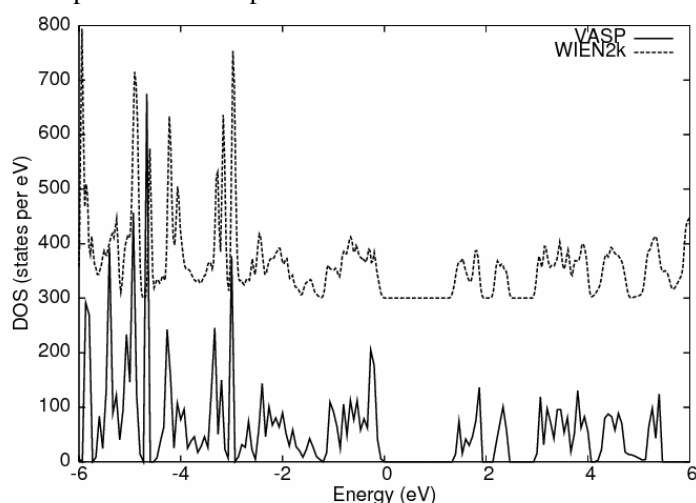


Figure 2: Total DOS calculated using the WIEN2k (dotted line) and VASP (solid line) codes.

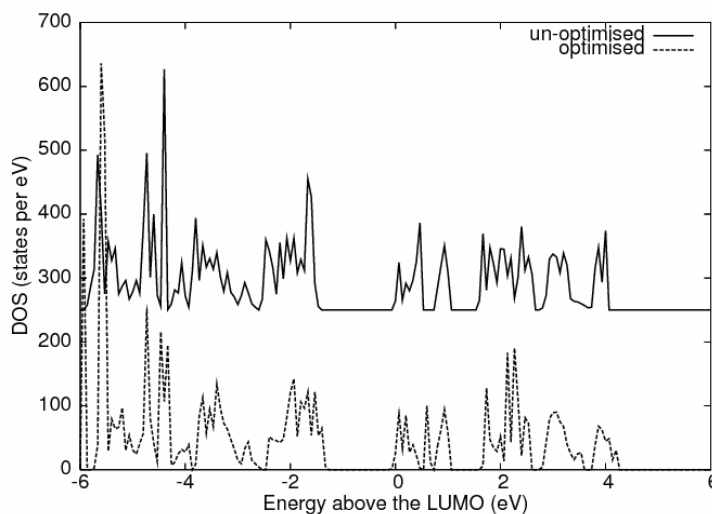


Figure 3: Total DOS for the un-optimised and optimised structures.

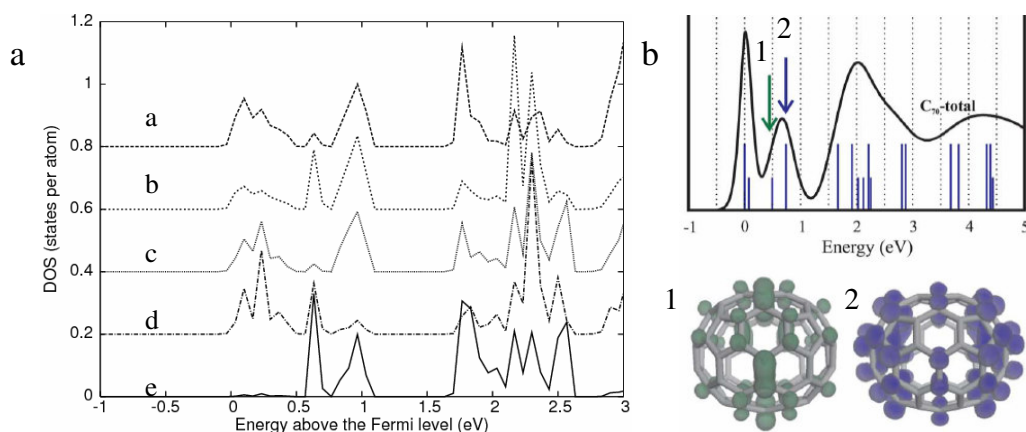


Figure 4: DOS from one atom in each of the five rings in the optimised structure (a) and the previous results from the molecular calculation (b).

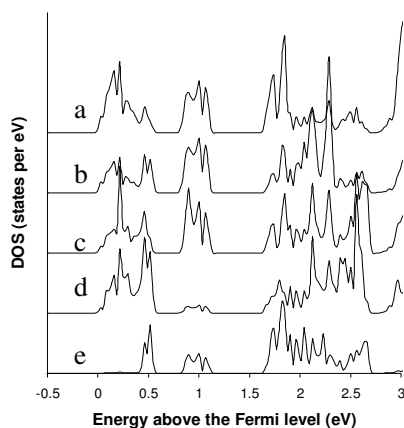


Figure 5: DOS from one atom in each of the five rings in the un-optimised structure.

5. Conclusions

In this paper we have shown that changes in the bond lengths within a C_{70} crystal can have an effect on the DOS. The differences in the DOS from un-optimised and optimised C_{70} crystal structures result from the differences in the bond lengths between the two structures. The optimised structure produces a DOS which is similar to that from molecular calculations, and so differences between the un-optimised structure and molecular DOS which have been reported previously are likely to be due to the differences in bond length.

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