

High Resolution X-ray Absorption Spectroscopy of the Polycyclic Aromatic Hydrocarbons

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Introduction

A high resolution X-ray absorption spectroscopy study of the polycyclic aromatic hydrocarbons has been undertaken using the SGM beamline 11ID-1. The four and five membered polyacenes, tetracene and pentacene, have been recognized as potentially valuable materials for the growing organic electronics industry. These materials show reasonable charge carrier mobilities

and self assembly properties that make them attractive for use in Organic Thin Film Transistors (OTFT's)[1,2]. The fundamental building block of the polyacenes, the hexagonal carbon ring, is also seen in many other interesting materials including carbon nanotubes and graphene. The goal of this project is to generate an understanding of the electronic and structural properties of materials constructed from these hexagonal carbon rings by studying the X-ray absorption characteristics of the polycyclic aromatic hydrocarbons as a function of their size. *Ab initio* calculations are used to aid in the interpretation of the data. To date, the linear polyacenes, benzene, naphthalene, anthracene, tetracene and pentacene have been measured and calculated.

Experiment

The NEXAFS spectra of benzene and naphthalene were recorded in photoionization yield from gas phase samples at room temperature. The anthracene, tetracene and pentacene samples were purified in a horizontal furnace and measured in the solid state, also at room temperature. Measurements were also made on samples of tetracene and pentacene prepared as thin films as described in [3]. All spectra were recorded using total electron yield (TEY) with the beamline configured for high resolution ($E/\Delta E > 12\,000$)[4]. The effects of carbon absorption by the beamline optics was accounted for by normalizing the electron yield from the sample to the electron yield of a freshly evaporated Au mesh. All spectra were calibrated using the $C\ 1s \rightarrow \pi^*$ ($\gamma = 0$) transition measured from CO gas.

The positions and intensities of the electronic resonances were determined using the STOBE version 2.2 code[5] using the procedure described in [6,7]. The results are shown in Figure 1.

Results and Discussion

Good agreement between the DFT calculations and the measurements are seen when purely electronic transitions are considered. The spectra show that transitions to the lowest

unoccupied and next lowest unoccupied molecular orbitals (LUMO and LUMO + 1) split in energy generating two π^* manifolds as the number of aromatic rings increase. The calculation results show how the manifolds are generated through the excitation of a progression of atomic sites. Transitions to the LUMO come from excitation of the end and peak atoms while transitions to the LUMO+1 occur from the excitation of any atomic site. This has been predicted previously by Agren et al; who employed *ab initio* static exchange calculations to model the electronic structure[8]. A distinct 3 peak feature, seen in the first manifold for naphthalene through pentacene, is generated by excitation of the end atoms. The difference in energy of these two end atom transitions decreases as the chain length increases. At the same time, the separation between the end atom transitions and the centre-peak atom transitions in the first manifold is growing.

The rich structure observed in these measurements is confirmed as vibronic in nature when the spectra are viewed as a series. In fact, the most striking result of these measurements is that vibronic structure is clearly resolved in the anthracene, tetracene and pentacene spectra. Observation of this vibronic coupling has been previously reported and studied in benzene and naphthalene [9,10], but were not expected to be as readily observed in the larger molecules in this series. As the size of the molecule increases it was thought that the high density of vibronic states, combined with an increasing core hole lifetime, would manifest as a continuum distribution in the XAS, rather than discretely resolved features [11].

The presence of the vibronic structure allows for further analysis of the core excitation processes in this series of molecules. As reported by Ma et. al. for benzene, the excitation of non-totally symmetric modes demonstrates the breaking of the ground state symmetry in the molecule due to the core level excitation as well as the extent to which a core hole is localized in the structure[9]. A detailed Franck-Condon analysis of the vibronic features in the larger molecules will determine what effect the core hole has on the symmetry of the larger molecules. With these measurements, this analysis can be done as a function of the number of hexagonal rings and the specific excitation site on the molecule.

Conclusion

At this stage of the project, we have demonstrated that high resolution gas phase and solid state measurements of the linear polycyclic aromatic hydrocarbons reveal a rich structure that is a combination of electronic and vibronic transitions. The electronic transition energies and intensities can be understood

within the framework of a DFT based model which predicts the evolution of the two distinct manifolds generated as the number of aromatic rings increases. The excitation site specificity afforded by the calculations shows that contributions from the end, peak and valley sites are sufficiently separated.

We have also demonstrated that vibronic features can be observed in the solid state spectra of anthracene, tetracene and pentacene. These features, upon further analysis, should provide details on symmetry breaking and core hole lifetimes in these molecules. This new information will be valuable in future studies of these materials, particularly tetracene and pentacene.

Work continues on this project, including the extension the measurements to larger molecules and the application of molecular dynamics simulation to the problem of understanding nuclear rearrangement. Gas phase absorption measurements of the larger molecules will be obtained and temperature dependence will be explored. A thorough investigation of the vibronic profile will be performed to determine to what level this fine structure can be used determine new information about the use of the linear polycyclic hydrocarbons as an active medium in organic electronic devices.

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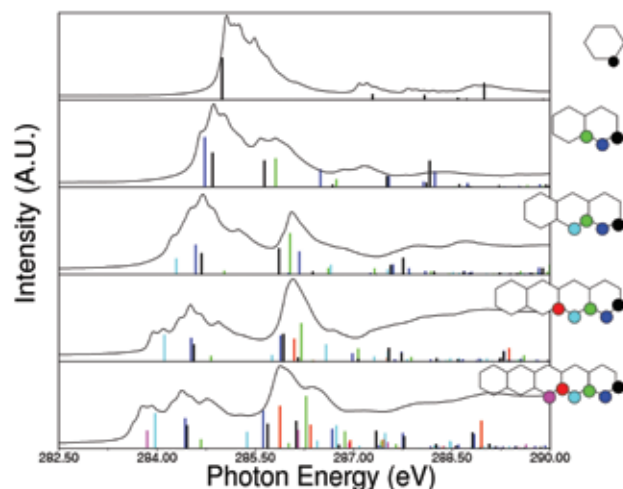


Figure 1: Carbon K edge NEXAFS spectra of the linear polycyclic aromatic hydrocarbons shown with calculated electronic transition energies and intensities. Atomic sites are defined as end atoms (black and dark blue), peak atoms (pink and light blue) and valley atoms (red and green).