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Theoretical x-ray absorption investigation of high pressure ice and compressed graphite

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Abstract

The x-ray absorption spectra (XAS) of high pressure ices II, VIII, and IX have been computed with the Car–Parrinello plane wave pseudopotential method. XAS for the intermediate structures obtained from uniaxial compression of hexagonal graphite along the *c*-axis are also studied. Whenever possible, comparisons to available experimental results are made. The reliability of the computational methods for the XAS for these structures is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The structures of water and amorphous ices have received a great deal of attention lately. The degree of tetrahedral coordination and the number of broken bonds in the models used to describe the structures has been under debate [1–8]. A recent report suggested that the water molecules in liquid water participate to a great extent in broken bonds [3]. This is contrary to the belief that water is primarily tetrahedrally coordinated. To date, the structure of water still remains unsolved. Experiments like O 1s x-ray absorption spectroscopy (XAS), which is a site-specific probe, are expected to provide insight into the electronic structure of liquid water. However, the origin of the remarkable results is not fully understood.

The analysis of the electronic structure from the water XAS depends heavily on comparison with theoretically calculated spectra. Calculations based on water structures derived from the trajectories of classical or *ab initio* molecular dynamics calculations failed to reproduce the observed spectra. The disagreement between theory and experiment may be due to the computational approach or the structural models or both. Since the structures of some high pressure ices are already well characterized [9, 10], an investigation into the origin of the absorption features in the XAS of these systems will provide important clues to the elucidation of the structure, bonding, and electronic structures of liquid water and amorphous ices.

It is well known that carbon can participate in sp, sp², and sp³-type bonds, and hence can exist in a variety of polymorphic forms. The conversion mechanism between various

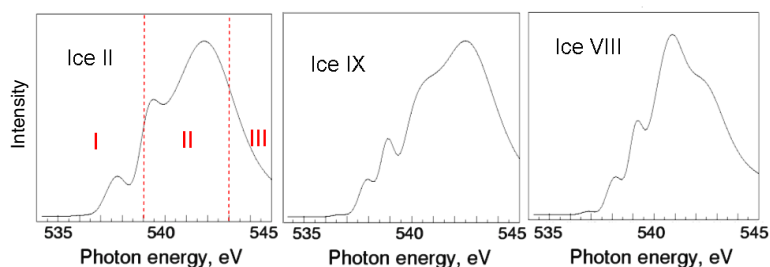


Figure 1. XAS for ices II, VIII, and IX computed with the HCH approach in CPMD. For the convenience of discussion, the XAS can be divided somewhat arbitrarily into three regions: the pre-edge (I), main edge (II), and post-edge (III).

forms of carbon has long been a topic of interest. Much of the work has been done on the conversion of graphite to diamond, but another intriguing pathway is the conversion of graphite to superhard forms of carbon. A recent experimental investigation [11] has shown that compression of graphite under the right conditions leads to a superhard form of graphite which is structurally different from the more well-known hexagonal diamond. Changes in the electronic structure on the formation of the new polymorphic phase have been monitored using inelastic x-ray scattering (IXS) experiments. In principle, IXS provides similar information to XAS but is amenable to an *in situ* study of materials in a diamond anvil at high pressures. However, as with hexagonal graphite and diamond, the assignment of the spectra features in the XAS are uncertain and is still being debated [11–15]. It is hoped that a comparison between calculated XAS with the experiment will gain new insights into the electronic structure and the transformation mechanism.

2. Theoretical method

In this work, the XAS of high pressure ices and the structures obtained for uniaxial compression of hexagonal graphite have been computed using the Car–Parrinello plane wave pseudopotential method CPMD [16]. Two approaches in mimicking the final state [17], the half core–hole (HCH) and full core–hole (FCH), were used to compute the near-edge XAS. For the ice structures, only the HCH results are presented, while for the graphite results from both methods are presented. The structure of high pressure ice II, IX, and VII were obtained from the experimental crystal structures. The graphite geometries were produced by optimization of the structures resulting from static compression along the *c* axis. XAS spectra were calculated from the calculated transition moments and convoluted with Gaussian functions. The procedure follows that described earlier; below onset of the ionization threshold, Gaussian functions with fixed width were used whilst energy dependent widths were used for the continuum states.

3. Results and discussion

The computed XAS of ices II and IX are compared with the experiments. So far, no experimental results exist for ice VIII. However, some structural comparisons to ices II and IX are made. Analysis is focused on three regions of the XAS: the pre-edge (I), main edge (II), and post-edge (III). Figure 1 shows the calculated XAS for ices II, VIII, and IX. Experimental results for ices II and IX have been reported in [1]. Comparison of the XAS for ices II and IX shows that the calculated spectra qualitatively reproduce strong absorption features near 538 eV

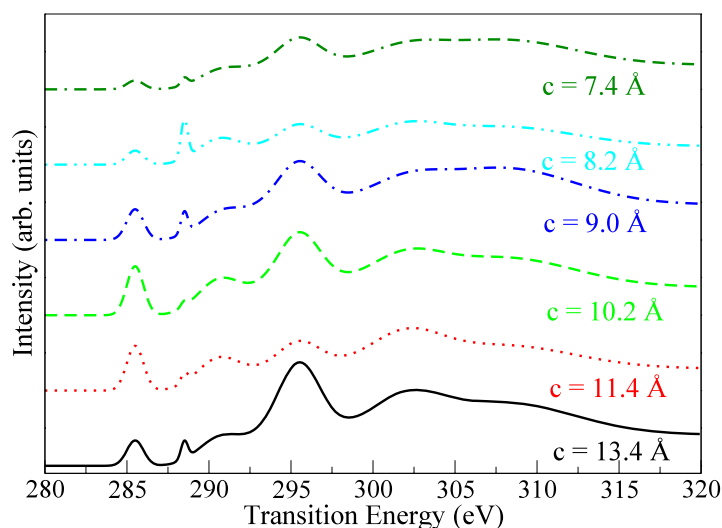


Figure 2. XAS for graphite along the compression path from hexagonal to superhard using the HCH approach in CPMD.

observed in the pre-edge region I. However, the agreement is not as good in the main edge (II) and post edge (III) regions. The discrepancy in the main and post edge regions is most likely due to the lack of proper continuum wavefunctions to describe the almost free electron states. Since the experimental resolution is very low, it is difficult at this time to make a definitive assessment on the reliability of the predicted XAS. Nevertheless, the CPMD method apparently is reliable for reproducing the features observed in the pre-edge region of the ice XAS.

Figure 2 shows the XAS for structures obtained from uniaxial compression of the c axis using the HCH approach. It is well known from the graphite to diamond conversion that as hexagonal graphite is compressed, increased interactions between carbon atom adjacent layers resulted in the formation of sp^3 σ bonds linking the layers. The formation of the sp^3 bonds is at the expense of the reduction in the sp^2 π -bonding within the layer. The weakening of π interactions resulted in the reduction of the intensity of the π^* peak (ca 286 eV) in the XAS. At the same time, the formation of σ bonding between the layers increases the intensity of the σ^* peaks in the XAS. This is indeed the trend observed in the theoretical spectra and the experiments. From figure 2, it is shown that as graphite is compressed the intensity of the low energy peak assigned to excitations into the π^* orbitals decreases gradually and, on the other hand, the intensity of the bands corresponding to the σ^* excitations increases substantially. This implies a reduction in the π bonding between the carbon atoms in the layers and reduced π interactions between the layers. This is combined with additional σ bonding between the layers. The structures obtained from the uniaxial compression along the c axis are shown in figure 3, and they clearly show the bonding changes expected from the results of the XAS. Thus, the trends expected in the XAS are correctly reproduced by the plane wave pseudopotential method. A detailed comparison of theoretical and calculated XAS shows that the peak height of the π^* excitation is seriously underestimated. The agreement with experimental spectra is at best qualitative. Another significant difference between the experiments and the present theoretical model is that the π^* peak in the experimental spectra has already disappeared at $c \sim 57$ Å (the unit cell was estimated from the observed (200) and (002) Bragg reflections) [11]. This is to be compared with the present model where the π^* component is still quite clear at

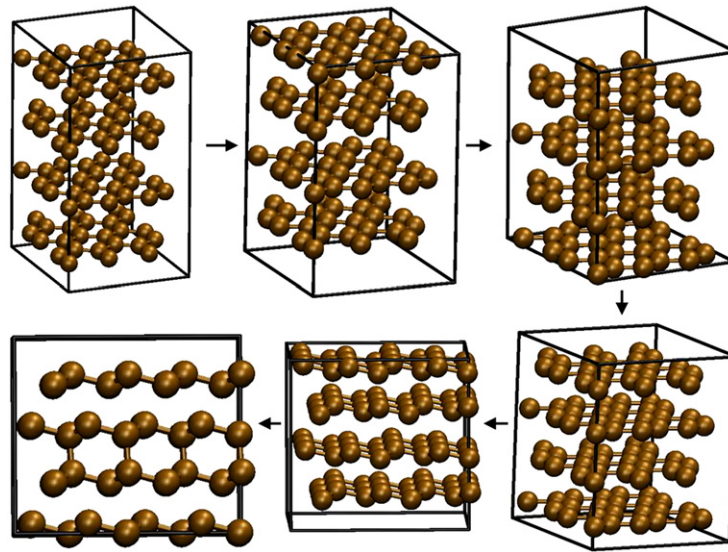


Figure 3. Structures obtained from uniaxial compression of the c axis of hexagonal graphite. The compression path follows the arrows shown in the figure from $c = 13.4 \rightarrow 11.4 \rightarrow 10.2 \rightarrow 9.0 \rightarrow 8.2 \rightarrow 7.4$ Å, leading from hexagonal graphite to a form where there is significant bonding between the layers.

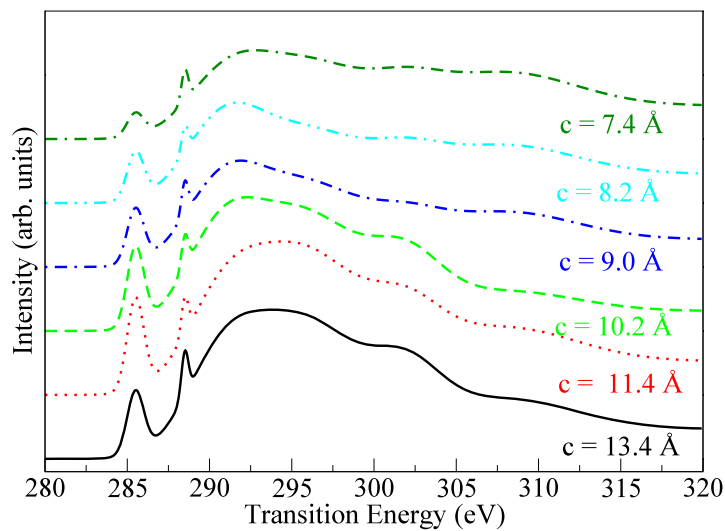


Figure 4. XAS for graphite along the compression path from hexagonal to superhard using the FCH approach in CPMD.

$c \sim 7.4$ Å. A detailed analysis of the theoretical results and comparison with the experiments will be published separately.

To investigate potential causes for the discrepancy between the theoretical spectra and experimental calculations along the compression pathway of graphite were repeated using the FCH approximation. Figure 4 shows the XAS obtained using the FCH approach. These spectra show the same trends upon compression as predicted in the HCH calculations, the computed

relative intensity between the π^* and σ^* peaks shows a marked improvement. Although the calculated XAS are still not in quantitative agreement with the experiments, the results show that the FCH method may likely be more appropriate to describe the XAS for graphite. The sensitivity of the calculated spectral features with the approximation for the core-hole state is problematic. In principle, the HCH approach, which satisfies the Slater transition state theory, should be theoretically more exact since the core relaxation effect is corrected to first order implicitly. Nevertheless, a direct comparison between calculated and observed spectra shows that, at this moment, there is apparently no preferred computational model for the accurate description of the XAS spectra that satisfies most systems. The theoretical reason behind the difference trend produced by the FCH and HCH calculations is under investigation.

4. Conclusions

In conclusion, the XAS for the ices II, VIII, and IX as well as for the uniaxial compression of hexagonal graphite are presented and compared to experiments. In all cases, general features, particularly in the pre-edge region are reproduced but quantitative agreement with observed spectra has not been achieved. For high pressure ices, the high energy spectral region beyond the ionization threshold is not described well with the present approach. This is likely to be the result of insufficient treatment of the continuum states. In the graphite system, the relative π^*/σ^* peak intensities are not reproduced with both the FCH and HCH approximations.

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