

(S)TEM Characterization of Functionalized Adamantanes by Low-Dose EELS and PDF Analysis in their Pristine and Laser-Irradiated States

Jürgen Belz^{1*}, Johannes Haust¹, Franziska Hüppe¹, Andreas Beyer¹ and Kerstin Volz¹

¹ Department of Physics and Materials Science Center, Philipps-University Marburg, Marburg, Germany.

* Corresponding author: juergen.belz@physik.uni-marburg.de

Based upon the discovery of a highly non-linear optical response, namely directional white-light emission found in tetraphenyl-tin-sulfide-clusters [1], we investigate structurally similar organic functionalized adamantanes (Ad) prior to and after laser exposure. In particular we analyzed tetraphenyl-Ad (Ph-Ad) as well as tri-bromo-phenyl-Ad (Br3Ph-Ad) which show different non-linear optical responses.

The goal of our study is to identify the local structure as well as chemical bonding by analyzing the pair distribution functions (PDF) and the electron energy loss spectra (EELS) of these materials in their pristine as well as laser and electron beam exposed states. Furthermore, we carry out density functional theory (DFT) for bond lengths and core electron energies determination and scattering simulations based on supercells of multiple Ad-based molecules that were energetically relaxed by molecular dynamics (MD).

In order to achieve high quality samples for Transmission Electron Microscopy (TEM) having a suitable thickness, we embedded the specimens in epoxy and cut them into 50 nm thick slices using a LEICA ULTRACUT UCT ultramicrotome (UMT).

The PDF measurements were carried out with a JEOL JEM-3010 TEM equipped with a TVIPS-XF416-ES camera. The EELS measurements were done with a double-aberration corrected JEOL JEM-2200FS (S)TEM that is additionally equipped with a PNDetector pnCCD direct electron camera with full frame rate of 2000 fps.

We find that the diffraction pattern (DP) of the pristine (i.e., non-irradiated) crystalline state of Ph-Ad undergoes a rapid change at doses as low as 20 e/A² and a full amorphization is observed at around 100e/A² almost identical for 300 kV and 200 kV electrons. The carbon K-shell ionization edge shows a strong degradation of the 1s-π* C=C associated peak at 285 eV and a broadening of the ionization edge suggesting the formation of different carbon bonds.

The primary loss of C=C bonds leads to the conclusion that the phenyl-group is predominantly affected, whereas the adamantane core is largely unaffected. This finding is supported by the absence of a single-electron transition at 6.5 eV in the electron and laser-irradiated specimen which is typically associated to C=C bonds [2]. The stability of the adamantane core is verified by PDF measurements (Fig. 1) which show the nearest neighbor (NN) and second NN (2NN) distances as predicted by scattering simulations from MD relaxed supercells. These distances are present even after laser and heavy electron irradiation.

The comparison of pristine Ph-Ad with the laser-irradiated state shows that structural amorphization and photochemical effects take place and alter the state of the material under investigation significantly. Additionally, we show that the laser irradiation in the case of Br3Ph-Ad leads to a significant loss of

bromine. In our studies, we find that the pristine (non-irradiated) state of Br3Ph-Ad is either extremely electron sensitive ($< 1e/A^2$) or largely amorphous before TEM investigations.

In figure 2 it can be seen that the sp^2 -peak ($1s-\pi^*$ C=C) at 285 eV is drastically reduced in the case of strong laser irradiation (red curve). It can also be seen that the sp^3 -peak ($1s-\sigma^*$ C-C) at around 293 eV and therefore the left side of the K-shell ionization edge is slightly shifted towards higher energies for pristine Br3Ph-Ad compared to purely organic Ph-Ad. These effects agree with DFT calculations that model the laser irradiation by electron-hole pair injection as well as the ionization energies.

At last, we compare first results using a direct electron detector for low dose spectroscopy enabling a convenient and dose efficient way of measuring EELS of very beam sensitive materials in non-specialized TEMs.

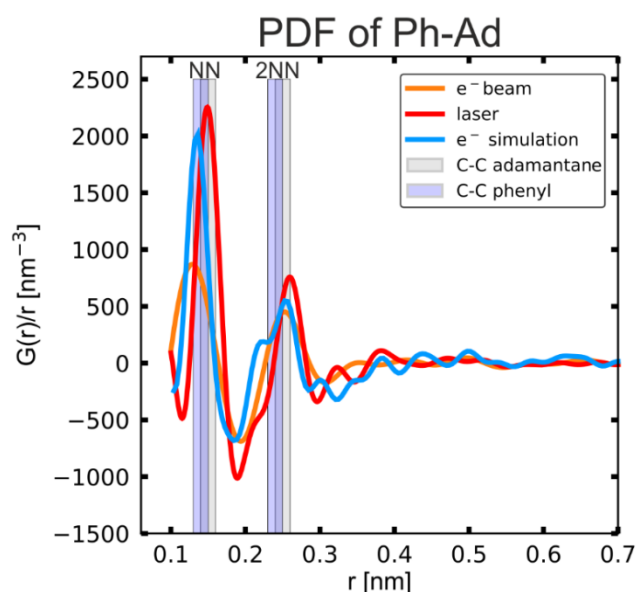


Figure 1. Pair distribution function of Ph-Ad in different states showing the qualitative agreement between the simulated PDF from scattering simulations based on MD supercells. The calculated NN and 2NN positions attributed to phenyl-group carbon atoms as well as carbon atoms from the adamantane are shown as vertical bars. Their width is connected to the accuracy of the measurement data.

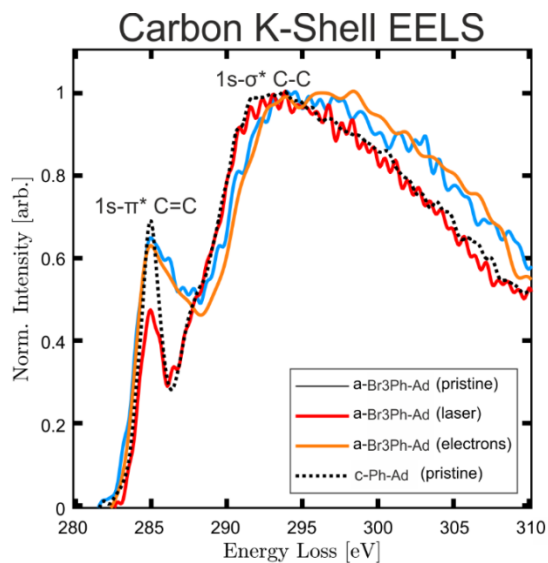


Figure 2. The EELS of the pristine and electron-irradiated specimens show a nearly identical behavior and a shift to higher energies with respect to the organic Ph-Ad. The laser-irradiated specimen shows a very different shape that follows the spectrum of Ph-Ad, except for a strong reduction in C=C bonds.

References:

- [1] Rosemann, N. W. et al., *Science* **352** (2016), pp. 1301–1304. DOI: 10.1126/science.aaf6138
- [2] E. E. Koch and A. Otto, *Opt. Comm.* **1** (1969), pp. 47–49. DOI: 10.1016/0030-4018(69)90003-0