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Study of oxygen-C_{60} compound formation by NEXAFS and RIXS

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Abstract. The interaction of oxygen with C_{60} molecules was studied on a C_{60} film which had been exposed simultaneously to oxygen and UV-light for 190 hours, producing an approximately $C_{60}O_1$ stoichiometry in the bulk of the sample. C K-edge and O K-edge NEXAFS (using total fluorescence yield detection) and resonant X-ray inelastic scattering (RIXS) spectra from the sample film were measured and the C K-edge data were compared to the spectra from pristine C_{60} as reference. The C K-edge absorption and emission spectral profiles of the oxygen-doped sample are similar to those of the C_{60} reference, suggesting that cage breaking of C_{60} under these conditions, if any, is negligible. However, the redistribution of intensities in the spectra indicates changes in the occupancies of different molecular orbitals, possibly due to changes in electron density upon reaction. Similarities of the O K-edge soft X-ray emission (SXES) spectra to several small oxygen-containing molecules is being discussed in terms of bonding models.

PACS. 73.61.Wp Fullerenes and related materials – 33.50.Dq Fluorescence and phosphorescence spectra – 33.20.Rm X-ray spectra

1 Introduction

The light-induced oxidation ("degradation") of C_{60} was first noted by Taylor *et al.* back in 1991 [1]. Since then, a number of publications have appeared which study both light- and heat-induced oxidation of C_{60}. In fullerite films, exposed to air, oxygen has been shown to not only adsorb to the surface, but also intercalate readily into the interstitial sites in the C_{60} crystal lattice [6,9]. Arai *et al.* [19] have reported large (*ca.* 4 orders of magnitude) increase in the resistivity of C_{60} upon oxygen exposure (intercalation), followed by a slight decrease after a heating cycle in vacuum to 630 K to desorb the oxygen. However, when annealing a C_{60} sample, the de-intercalation of the contained oxygen competes with further reaction of oxygen with the fullerite, which ultimately leads to the opening and breaking of the C_{60} cages [2,20]. The processes are similar when the sample is exposed to UV-light [3,21,22] instead of heating. On the other hand, it has been observed that bonded oxygen stabilises the C_{60} against the polymerisation of C_{60} at elevated temperatures [3]. In that light, the reported decrease of resistivity might be an indication that oxygen reacts with C_{60} resulting in partial electron transfer, a process which in view of the known large electronegativity of the fulleride seems probable.

Simple geometric considerations – the effective radii of the octahedral (4.15 Å) and tetrahedral (1.12 Å) voids and the oxygen molecule (1.4 Å) suggest that oxygen would preferably occupy the octahedral sites, assuming that the O_2 does not dissociate. TDS measurements in Ref. [17] using labelled $^{18}O_2$ support the view that dissociation is not taking place, suggesting that the limiting stoichiometry of the $C_{60}O_x$ (without cage breaking) is $x = 2$, which corresponds to six O_2 molecules adjacent to a C_{60}. This agrees with the NMR results in Refs. [6,9,16], where exactly 6 new peaks appear upon oxygen exposure ($x < 2$).

We are here presenting results of an X-ray emission and absorption study on a $C_{60}O_x$ film sample, which was obtained by exposing a pristine fullerite film to UV-light in air. The composition of the film was determined to be close to $C_{60}O_1$ in the bulk of the sample, corresponding to filling approximately half of the octahedral lattice voids.

2 Experimental

The measurements were carried out at beamline 7.0.1 at ALS, LBNL, Berkeley, CA. The experimental resolving power E/ΔE was set to approximately 1000 for both the monochromator and the spectrometer when measuring the SXES spectra in both energy windows (C and O K-edges). Resolving power was set to 2000 for taking the NEXAFS spectra. X-ray emission was detected using a grazing incidence grating spectrometer (Grace) [4], which includes three spherical gratings, and an MCP-detector with position-sensitive readout, mounted in Rowland circle geometry. A 1200 l/mm and a 400 l/mm grating were used for measuring the O K-edge and the C K-edge emission, respectively. The sample C_{60} film was deposited onto

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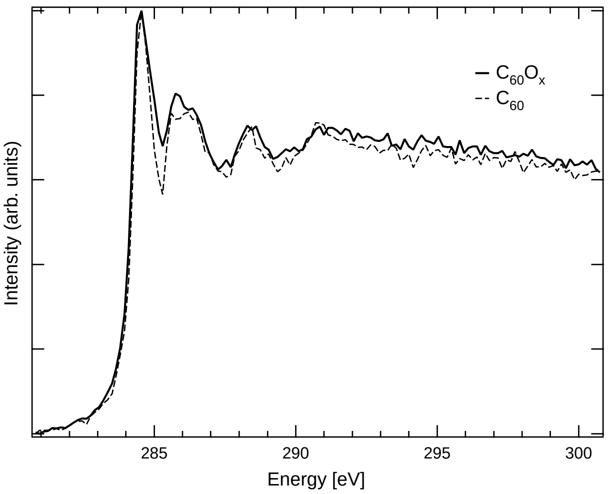

Fig. 1. C K-edge X-ray absorption (NEXAFS) spectra of $C_{60}O_x$ and C_{60}, measured in total fluorescence yield (TFY) mode.

a H-terminated Si(100) substrate at room temperature in UHV. The C_{60} was evaporated during 20 minutes at 500 °C evaporator temperature. Due to the high deposition rate, the crystallite size within the film is relatively small (*ca.* 170 Å). The deposited film was exposed to UV-light from a 300 W Hg-lamp for 190 hours at RT [3]. The stoichiometry of the oxygen-doped fullerite film $C_{60}O_x$ was determined by XPS sputter depth profiling to be approximately $C_{60}O_{0.9-1.05}$, except for a *ca.* 20 Å surface layer, where the oxygen content was high ($x = 14.5$). The obtained low x stoichiometry in the bulk is similar to the results by Gu *et al.* [5] which describe a decrease in oxygen content in a fullerite film upon long exposure after reaching an initial maximum. Although the surface composition is different, the penetration depth of the X-rays is on the order of at least 1000 Å, and the SXES spectra here display the bulk information (signal from the oxygen-rich surface layer is not more 2-3% in the C K-edge spectra and below 20% in the oxygen K-edge spectra).

3 Results and discussion

The soft X-ray emission (XES) and resonant inelastic scattering (RIXS) process, the spectral profile is determined by the partial electronic density of states and the dipole selection rules. This means that different from the photoelectron spectroscopies that provide information on the total density of states in the valence band, the XES and RIXS are capable of providing symmetry-selective, element-specific information of the valence band. Due to vibronic coupling in the intermediate (*i.e.* valence) state, the symmetry-selectivity may become less strict, though, which is clearly the case for C_{60} (see, *e.g.* [14]). However, by detuning the excitation energy below the 1*s*-LUMO absorption resonance, the interaction time is reduced and the symmetry-selectivity is restored [15].

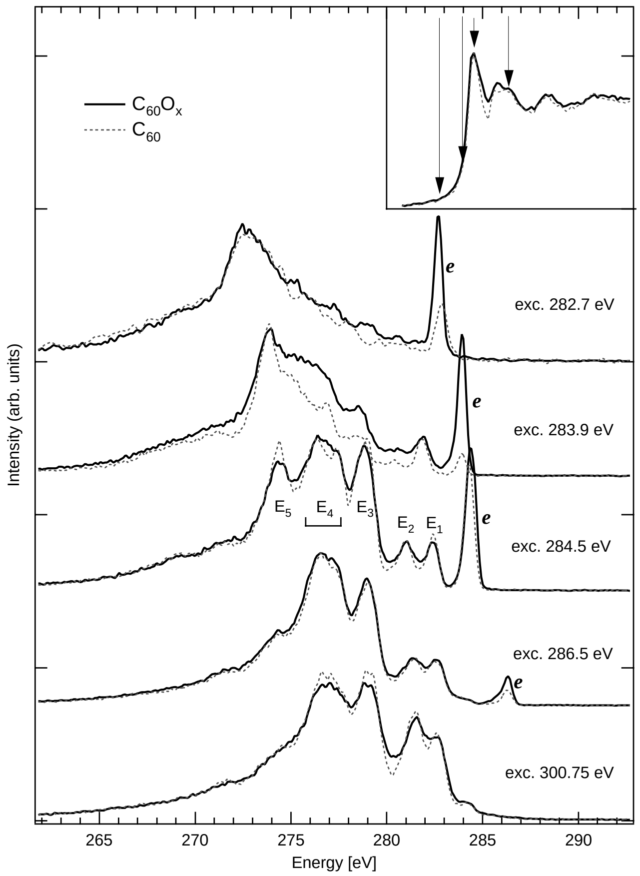

Fig. 2. C K-edge SXES spectra, excited at different photon energies, as indicated by numbers at the right of each spectrum and by arrows on the absorption curve (inset at top right). The peak marked with *e* is the elastic scattering of incoming light.

Compared to C_{60}, the C K-edge absorption and emission spectra (see figures 1 and 2) of the C_{60}-oxygen compound are broadened, and the relative intensities of the spectral lines show excitation energy dependent differences from the pristine material. In C 1*s* absorption, convoluting (broadening) the C_{60} spectrum by a 0.35 eV Gaussian gives a close fit to the $C_{60}O_x$ spectral profile, apart from a slight (5%) decrease of the LUMO intensity for the oxidised sample. In the X-ray emission (and scattering) spectra, the broadening of spectral features has some dependence on excitation energy, decreasing quasi-monotonously from 0.8 eV in the non-resonant (fluorescence) spectrum with excitation energy 300.75 eV to *ca.* 0.45 eV in the 1*s*-LUMO resonantly excited spectrum. In the RIXS spectrum, excited at 282.7 eV (corresponding to the energy separation between 1*s* and HOMO, 1.8 eV below the π^* absorption resonance), the spectral profile seems to be even sharper for $C_{60}O_x$ having less intensity in the low energy tail of the spectrum below 274 eV, although the statistics does not allow to be conclusive. Relative intensities are also energy-dependent: there is no difference from C_{60} for excitation energies from LUMO+1 and up, but at 1*s*-LUMO (π^*) resonance and 0.6 eV below it the emission feature E_5 at 274.5 eV is clearly (15-20%)

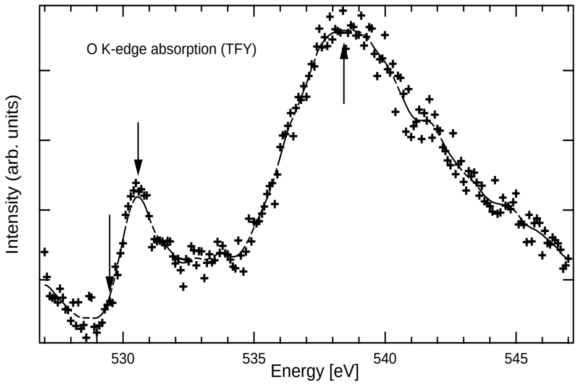

Fig. 3. O K-edge NEXAFS spectrum of $C_{60}O_x$, measured in TFY mode. Dots - experimental data, the line (smoothed spectrum) is a guide for the eye. Arrows indicate the excitation energies of the emission spectra.

depleted. At the same time, the features E_3 and E_4 are enhanced, especially in the detuned spectrum. A possible explanation of these effects can be enhanced vibronic coupling through the oxygen sites (it has been noticed that the oxygen, diffusing readily into fcc octahedral voids in C_{60} lattice, couples to the lattice modes [6]). On the other hand, assuming that O_2 intercalates into the lattice without dissociating [6,9], roughly only half of the octahedral voids were populated by O_2, and the local electronic structure varies considerably, which possibly results in several nonequivalent carbon sites with slightly shifted electronic energy levels.

The latter viewpoint seems to be in better agreement with our observation of the unusually large broadening of lines in nonresonant SXES at O K-edge, which points to that probably oxygen has a number of different next nearest neighbour configurations which are shifted in energy. Comparison of the low, but existing π^* peak and the intense σ^* profile in the O K-edge absorption curve in figure 3 to the spectra of small oxygen- and carbon-containing small molecules [18] does not give a unique answer, but shows similarities to carbon-oxygen double bond in carbonyls or ketones. The energy of the broad σ^* feature is similar to alcohols, although IR-spectroscopy results from a heat-treated sample (with a NEXAFS profile that is comparable to our data) in Ref. [7], do not show any evidence of C-H or O-H stretch modes, which are normally very intense.

The O K-edge SXES spectra (figure 4) excited at the π^* absorption resonance seem to be site-selectively excited, and the observed spectral features are similar to these of CO_2 spectra, whereas the spectra do not resemble to CO and O_2 SXES at O K-edge [11–13].

4 Conclusions

The electronic structure of $C_{60}O_x$ films has been investigated by X-ray absorption and emission (inelastic scattering) spectroscopies. The O K-edge NEXAFS data are comparable to the results, published in Refs. [2,7] on a fullerite film, heat-treated in oxygen at 500 K. The C K-edge absorption and emission lines are broadened and relative intensities, corresponding to different molecular orbitals, are to some extent redistributed. The spectra still retain the C_{60} spectral profile, which indicates that C_{60} cages have not been broken. The degree of line broadening in the nonresonant $C_{60}O_x$ O K-edge emission is extraordinarily large; a possible reason for this might be the presence of octahedral sites with different next-nearest neighbour O_2 coordination.

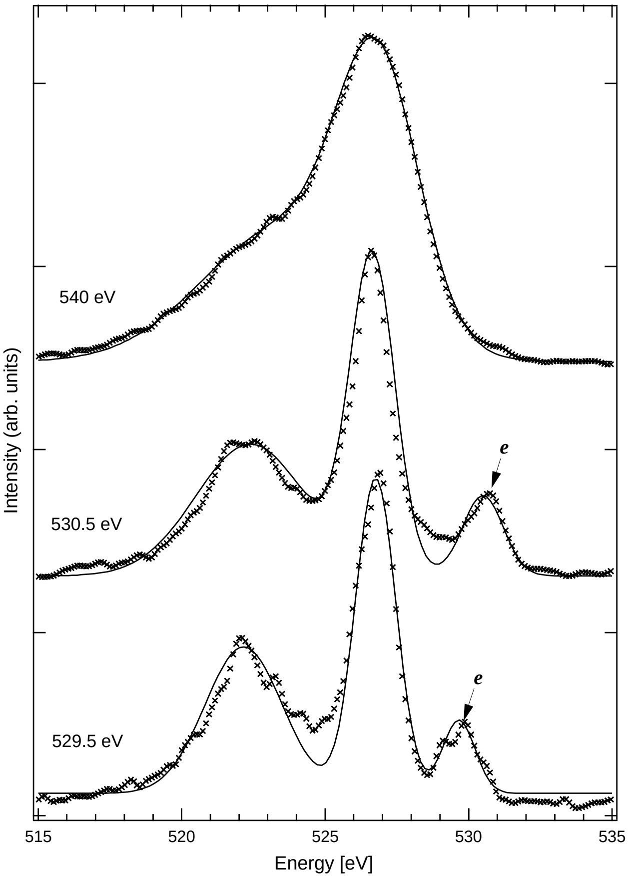

Fig. 4. O K-edge SXES spectra, excited at indicated photon energies. Peak "*e*" is the elastic peak. The line is a fit to the data using two Gaussian peaks at 522.2 and 526.7 eV, respectively, with varied linewidths at different excitation energies.

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