Single atom spectroscopy: decreased scattering delocalization at high energy losses, effects of atomic movement and x-ray fluorescence yield

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Abstract

Single atom localization and identification is crucial in understanding effects which depend on the specific local environment of atoms. In advanced nanometer scale materials, the characteristics of individual atoms may play an important role. Here, we describe spectroscopic experiments (electron energy loss spectroscopy, EELS, and Energy Dispersed X-ray spectroscopy, EDX) using a low voltage transmission electron microscope designed towards single atom analysis. For EELS, we discuss the advantages of using lower primary electron energy (30 keV and 60 keV) and higher energy losses (above 800 eV). The effect of atomic movement is considered. Finally, we discuss the possibility of using atomically resolved EELS and EDX data to measure the fluorescence yield for x-ray emission.

Keywords: EELS, EDX, STEM, Single atoms

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1. Introduction

Single atom identification has been a recurring theme in condensed matter physics and material science [? ? ? ?]. The ability to control single atoms or point defects increases the need to correctly identify the local crystal and
5 electronic structures of these entities. Quasi-elastic electron scattering imaging

(annular dark field images, ADF) using a focused electron probe in a scanning electron microscope (STEM) allows the localization of single heavy atoms inside a lighter matrix, such as Sb atoms in Si [?]. Scattered intensity is proportional to the atomic number, Z , [? ? ?] allowing atoms identification in propitious cases [? ? ? ?]. Electron energy-loss spectroscopy (EELS) [? ?] and energy dispersed X-ray spectroscopy (EDX) [?] are techniques that allow the identification of atomic species in a material based on their spectroscopic signatures. EELS may also give information about the local crystal and electronic structures of the probed species [? ?]. Single atom identification using EELS has been a reality for over a decade [? ?]. EDX single-atom identification has also been recently demonstrated [? ?].

In EELS experiments, delocalization effects limit the spatial resolution attainable for a given energy loss and electron probe primary energy, E [? ? ?]. The benefits of using lower electron probe energy are well known and have been demonstrated [? ? ? ?]. Moreover, the use of higher energy losses decrease delocalization. For example, for lanthanide atoms N -edge absorption edges (between 100 eV and 250 eV) are typically used for identification. Spatially resolved spectroscopy using those edges results in spatial resolution of the order of 3 Å ref. [?]. The use higher energy losses (M edges, above 800 eV) results in increased spatial resolution [? ? ? ? ? ?].

Here we report spectroscopic experiments (EELS and EDX) performed on lanthanide atoms trapped inside C₈₂ fullerenes loaded in carbon nanotubes (peapods of La, Ce and Er), molecules known as metallofullerenes [?] and in europium (Eu) chains confined inside carbon nanotubes [?]. We describe the benefits of lowering the energy of the probe electrons (Sections 3.1 and 3.2) for EELS experiments. This is followed by a description of the effects of atomic movement (Section 3.3) in EELS data acquisition. Specifically, a fortuitous benefit of delocalization is analyzed (Section 3.3). Parallel EELS and EDX measurement from single atoms is described in Section 3.4. These experiments have allowed an estimation of the fluorescence coefficient for the M edge of Eu atoms. Finally our conclusions are stated in Section 4.

2. Methods

High spatial resolution EELS experiments at 30 keV and 60 keV (electron beam primary energy) have been performed on a JEOL 2100F microscope equipped with JEOL Delta aberration correctors (dodecapole type) and cold field emission gun. A Gatan Quantum spectrometer modified for low energy operation has been used. The typical electron beam current at 30 keV and 60 keV was of the order of 20 pA. The probe convergence semi-angle was 40 mrad and 48 mrad at 30 keV and 60 keV, respectively. ADF inner detection semi-angle was 100 mrad at 30 keV and 60 keV, respectively. EELS collection semi-angle was 63 mrad and 59 at 30 keV and 60 keV, respectively. EELS exposure times of the order of 10-50 ms for N edges and 50 -100 ms for M edges. In the EELS filtered maps shown, background contribution was estimated using a power law and two 50 eV (15 eV) wide windows while the edges signal were measured in a 50 eV (15 eV) wide window for the M (N) edges.

Parallel EELS and EDX experiments at 60 keV have been performed in an ARM200F equipped with a Shottky field emission gun and CESCOR CEOS aberration corrector (hexapole type). A Gatan Enfina spectrometer has been used for EELS. For EDS experiments a Silicon Drift Detector (SSD) with 100 mm² active detection area (Centurio, JEOL) has been used. The detection solid angle, defined by the device geometry in the microscope, is 0.80 sr. The typical probe current was 70 pA.

Two kinds of samples have been used. The first one was formed of single Lanthanide atoms trapped inside C₈₂ fullerenes. Three different types of atoms have been used: lanthanum (La, $Z = 57$), cerium (Ce, $Z = 58$) and erbium (Er, $Z = 68$). The C₈₂ molecules containing single atoms have been co-doped into single-wall carbon nanotubes (SWNT) [?]. The second sample used was composed of europium (Eu, $Z = 63$) double atomic chains confined inside double-wall carbon nanotubes (DWCNT)[?].

For La and Ce, N and M EELS measurements at 60 keV can be performed in parallel. For the other atoms and for the experiments at 30 keV, N and

M measurements have been performed in series. The limitation for these experiments is the minimum dispersion possible of the energy spectrometer (300 meV/channel and 500 meV/channel at 30 keV and 60 keV, respectively)

70 Where noted, the following kernel was used to smooth images: $\{1, 2, 1; 2, 4, 2; 1, 2, 1\}$.

3. Results

3.1. Single atom spectroscopy using 60 keV and 30 keV electrons

EELS has been performed at 60 keV (Fig. 1) and 30 keV (Fig. 2) on single lanthanide atoms (La, Ce and Er) confined in C_{82} molecules which have been
75 co-doped in SWNT. An ADF image of the resulting structure is shown in Fig. 1a, where the heavy atoms appear as bright spots and the supporting carbon structures appear grey. Single atom spectroscopy can be performed either using the $N_{4,5}$ or the $M_{4,5}$ edges for lanthanides. Single atomic column $N_{4,5}$ and $M_{4,5}$ comparisons have been performed in the past [? ? ?]. Here, we show $N_{4,5}$ and
80 the $M_{4,5}$ in one of the thinnest possible samples, where electron propagation effects plays a minor role.

The $N_{4,5}$ edges occur due to energy absorption events from electrons in the 4d levels and appear in the 100 – 200 eV energy range. Their energy values for the atoms used in the experiments reported here are: La $N = 117$ eV, Ce
85 $N = 121$ eV, Eu $N = 133$ eV and Er $N = 164$ eV ref. [?]. These are delayed edges, with a spreadout energy-threshold caused by the orbital momentum of the initial state [?]. For this reason the determination of the energy threshold may be hindered by the background and noise. The $M_{4,5}$ edges have a smaller delocalization due to their higher energy thresholds, appearing between 800 eV
90 and 1600 eV. These edges occur due to transitions of electrons in the 3d levels. One important advantage of $M_{4,5}$ edges is the presence of characteristic sharp peaks known as white lines [?], which appear due to 3d→4f transitions. In lanthanides, with the exception of Lutetium, a high density of unoccupied 4f levels exist, explaining the high probability of losses observed [?]. The energy

95 for the M_5 edges white line peak for the atoms used here are: La $M = 832$ eV, Ce $M = 881$ eV, Eu $M = 1128.5$ eV and Er $M = 1410$ eV [?].

The benefits of performing single atom detection using these higher energy losses are greater spatial resolution (decrease delocalization, as described in Section 3.2) and higher energy separation between signals of different atoms preventing edges superposition (Fig. 1b). Energy shifts of the white lines allow
100 the distinction of difference valence state of lanthanides [?], even at atomic resolution [?]. For these reasons, whenever possible, $M_{4,5}$ should be preferred.

Because of detectors limitations, reduced total electron probe current in a subnanometer probe and to minimize the total electron dose, $N_{4,5}$ edges have
105 been used for lanthanides identification [? ?] due to larger cross section at lower energy losses. Two-dimensional (2D) mapping of $M_{4,5}$ signal has been used to detect small quantities of La in [?] and Sm in CeO particles [?]. Our results confirm, as was already know from previous experiments [?], that single atom identification and 2D mapping using $M_{4,5}$ edges is possible at high
110 spatial resolution (of the order of 1 Å, as discussed in Section 3.2) and high speeds (exposure times of the order of 50 ms or faster).

Fig. 1c-e shows a typical result for La, Ce and Er identification at 60 keV using $M_{4,5}$ edges (blue, green and red, respectively in the color map) . In Fig. 1b, spectra of La, Ce and Er are shown (summed over 9 pixels for La and Ce
115 and 16 pixels for Er).

It is known that lanthanide atoms are free to move inside C_{82} . This movement is increased due to the influence of the 60 keV electron beam. For this reason, extra atoms are seen (e. i. atoms which were not present before spectrum image acquisition, Fig. 1c) in the ADF image acquired in parallel to the
120 2D map acquisition . For example, two pairs are pointed by arrows in Fig. 1d-e. These extra atoms could have appeared due to movement of the same atom inside of the C_{82} . However, the EELS signal clearly shows them to be different: the first pair is Ce-La and the second one Ce-Er. These atoms came from elsewhere, demonstrating the necessity of spectroscopy to identify atoms
125 (as their atomic numbers are too close to prevent discernment by ADF con-

Figure 1: Single atom spectroscopy at 60 keV. (a) Typical ADF images showing the lanthanide atoms (bright spots) confined inside C₈₂ fullerenes, which were co-doped in SWNT. (b-d) 2D EELS mapping of the M edges shown in (e). (b) ADF image before EELS acquisition and (c) is the ADF during EELS acquisition. (d) Color-coded image showing the position single La (blue), Ce (green) and Er (red). Two pairs of atoms described in the text are pointed by arrows in (d). The acquisition time per pixel was 50 ms for this map. (c) and (d) have been smoothed. (e-f) Single atom spectra (marked by white squares in e)) for the M and N edges, respectively, of La (blue), Ce (green) and Er (red). The total exposure times for the M spectra were 450 ms for La and Ce and 800 ms for Er.

trast). Furthermore, this shows that these are not multiple images of the same atom oscillating, which can also be observed [?], as described in Section 3.3.

Substantial damage can occur to fullerenes under irradiation from a 60 keV or above electron beam [? ?], even though this energy is below the knock-on threshold for Carbon. Evidently, a smaller influence from the electron beam is desirable. Electron microscopy experiments at 20 keV [?], 30 keV [?] and 40 keV [?] creates significantly less damage and atomic natural movement (not induced by the electron beam) may be observed in specific situations. This decrease in damage is true for system in which knock-on plays an important role.

Indeed, we have observed significantly less damage for the fullerene sample at 30 keV. However, atomic movement cannot be suppressed. In Fig. 2 one example of single atom identification using the $N_{4,5}$ at 30 keV is shown. The C_{82} molecules show their original shape even after several 2D maps acquisition. In fact, a double image of an atom can be seen even in the 2D map (arrow in Fig. 2b). The two images are separated by 0.2 nm. However, an accurate measurement of the distance between the stable positions is not possible as it depends on the angle between a line joining the atomic pair and the electron beam (which we cannot estimate). The reason behind this double image is either the movement of the atom inside the C_{82} molecule, or a movement of the system as a whole (the C_{82} and the atom). Usually, such states are observed in images (acquisition time of the order of tens of μs) but not in the 2D chemical maps at 60 keV (Section 3.3). The exposure time for this 2D chemical map was 10 ms per pixel. Fast acquisition was possible due to the higher inelastic cross section at lower energy-loss and electron primary energy.

In the same 2D EELS mapping the carbon K edge (threshold around 284 eV) could be acquired in parallel. A map of this edge distinctly shows the contrast from the fullerenes shell (Fig. 2d). A hindrance to 2D chemical mapping of many atomic species at 30 keV is the limited energy range available to EELS. This happens due to the minimum natural dispersion of the energy spectrometer used. For this reason $M_{4,5}$ mapping of La, Ce and Er is not possible in parallel.

Figure 2: Single atom spectroscopy at 30 keV. ADF images acquired before (a) and during (b) the 2D EELS map acquisition. (c) Color-coded La (blue), Ce (green) and Er (red) N edge maps. The exposure time per pixel was 10 ms. (d) C K edge map, distinctly showing the contrast from the fullerenes. (e) spectra from La (blue), Ce (green) and Er (red) N edges averaged over 25 pixels (total acquisition time 250 ms). (b-d) have been smoothed

However, this is feasible in series of measurements. Finally, as explained in detail in Section 3.3, atomic movement happens continuously in this system. This greatly limits our capabilities for 2D mapping, as it poses an upper bound
160 on the typical exposure time before the system changes. Typically, we have used acquisition times of the order of 50 ms to mitigate this effect.

3.2. Decrease in inelastic scattering delocalization: effect of energy loss and primary electron energy

The spatial resolution of 2D EELS map is fundamentally limited by the
165 delocalization in inelastic scattering [? ? ?]. Delocalization occurs because of the non-zero probability of energy loss at impact parameter b . Essentially, the probability of energy loss decreases as $\exp(-2b/b_{max})$ for $b > b_{max}$ and as $1/b_{max}^2$ for $b < b_{max}$, ref. [?]. b_{max} is given by:

$$b_{max} = \frac{2\pi\hbar v}{\Delta E}, \quad (1)$$

where b_{max} gives the spatial extent of the delocalization and the limit for the
170 resolution in 2D mapping. This quantity depends on the energy loss (ΔE) and incident electron primary energy (E through v , the electron speed, in equation 1). However, comparison with experiments shows that such reasoning leads to predictions larger than the observed values. The reason for this is the extended angular distribution of inelastic scattering [? ?]. Egerton [? ?] has predicted
175 that the image of an atom should have a width at 50 % intensity equal to:

$$d_e(\Delta E) = \frac{\lambda}{2} \left(\frac{2E}{\Delta E} \right)^{\frac{3}{4}}. \quad (2)$$

The effect of delocalization can be clearly seen in the Fig. 3a-d, which shows the spatial distribution of the inelastic scattered intensity at two energy losses, the N edge at $\Delta E = 125$ eV, the M edge at $\Delta E = 881$ eV and their profiles at $E = 60$ keV, for two Ce atoms. This difference can be quantified from the
180 position at which the intensity has dropped to 50% in the loss maps. This position can be measured from profiles of the ADF and EELS maps (Fig. 3d).

At 60 keV the measured values are (0.15 ± 0.02) nm, (0.32 ± 0.02) nm and (0.20 ± 0.02) nm, for the ADF, $\Delta E = 125$ eV and $\Delta E = 881$ eV, respectively. From equation 2 the theoretical values for 60 keV are $d_e(125\text{eV}) = 0.42$ nm and $d_e(881\text{eV}) = 0.10$ nm. The measured value for $d_e(125\text{eV})$ is significantly
185 smaller than the theoretical one. We do not have a solid interpretation for this difference, but it might be due to convergence and collection angles effects which are not considered in our simple calculation. The $d_e(881\text{eV})$ is larger than predicted, which occurs because of the finite electron probe size. The decrease
190 in delocalization due to higher energy loss is evident in Fig. 3b-c. The resolution in the $\Delta E = 881$ eV 2D map is sufficient to discern the effect of a jump of the Ce atom closer to the bottom of the image (pointed by arrows in Fig. 3a and 3c). This jump appears only as a blur in the $\Delta E = 125$ eV image. Such jumps are inevitable, as described in Section 3.3.

For 30 keV electrons delocalization should be smaller, as seen in equation
195 2. The theoretical values are $d_e(125\text{eV}) = 0.36$ nm and $d_e(881\text{eV}) = 0.08$ nm. The $\Delta E = 125$ eV and $\Delta E = 881$ eV could not be measured in parallel and have been measured sequentially. The delocalization values at 50% intensity are: (0.36 ± 0.02) nm, (0.30 ± 0.04) nm, (0.34 ± 0.02) nm and (0.38 ± 0.02) nm,
200 for the $\Delta E = 125$ eV, ADF_{125eV}, $\Delta E = 881$ eV and ADF_{881eV}. No reduction in delocalization has been observed with the increase in energy loss at 30 keV. There are two possible explanations to this effect: the probe size is larger than the delocalization value or atoms show greater mobility (Section 3.3); in any case the overall effect is a blurring of the signal. This is corroborated by the
205 fact that the ADF and $\Delta E = 881$ eV profiles are broader than in the 60 keV case.

3.3. Atomic movement in metal fullerenes: effects of delocalization

It is known that a lanthanide atom can have more than one stable equivalent position inside a C₈₂ molecule, in absence of external influences [?]. At room
210 temperature, translation between these positions can be thermally activated. Translation occurs in time scales much shorter than typical exposure times in

Figure 3: (a-c) ADF and chemical maps at two different energy losses (125 eV and 881 eV) for two Ce atoms. The EELS maps have been made close the threshold energy for the *N* and *M* edges of Ce. Note that the spatial resolution in (c) is similar to that in (a). The broadening in (b) happens due to inelastic scattering delocalization. (d) comparison of the ADF, Ce *N* and Ce *M* signals at 60 keV. The difference in delocalization at two energy losses is clearly seen in (d). (a-c) have been smoothed.

ADF imaging (tens of μs). Hence, a hopping atom appears as multiple atoms (multiple images of the same atom) with reduced total intensity, as shown in Fig. 4a-d. In Fig. 4a two pairs of images with half intensity when compared to a stable atom are seen (profiles in Figure 4c). In Figure 4b a pair of images of a moving atom is seen close to a real pair of stable atoms (profiles in Fig. 4d). Multiple images of the same atom due to this effect have been reported before [?]. We should note that the transition time must be much shorter than scan time of a few pixels. If the oscillation time was much longer alternating darker (no atom) and brighter pixels should be seen. Indeed such behavior can also be found in this system. One example is shown in Fig. 2b (lower part), where the center portion of a C_{82} appears significantly darker than its upper and lower portions.

Transitions between hopping and a single stable position are routinely observed in this material. This occurs probably due to geometric changes of the C_{82} molecule induced by the electron beam.

In our experiments at 30 keV we have been able to measure the spectroscopic signature of hopping atoms. An example is shown in Fig. 2b, where a double image of an atom is seen. EELS showed that the atom was a Ce (not two lighter atoms, for example), confirming that the decrease in intensity was due to translation.

The EELS signal can also be used to detect and identify atoms which cannot be imaged in ADF images due to movement. In Fig. 4e we show an ADF image acquired prior to 2D EELS mapping in a region containing two atoms (in the marked rectangle). During mapping one of the atoms cannot be seen in the ADF image acquired and it seems to have left the C_{82} (Figure 4f). However, both atoms can be detected in the 2D $N_{4,5}$ EELS map (Fig. 4g). The upper one is a Ce and the lower one a La (confirmed by a successive $M_{4,5}$ EELS map).

Although more spread out, the total intensity of the integrated spectrum of the Ce and the La atoms is not significantly different. However, the "local" intensity is indeed different: for a given region the signal for the Ce atom is twice as large as for the La atom. This decrease in intensity is expected when compar-

Figure 4: (a-b) ADF images comparing atoms with two stable positions (1, 2 and 6) with those with one stable position (3,4 and 5). The distinction can be made based on the ADF intensity. This can be seen in more detail in the profiles shown in (c-d). (e-g) 2D EELS map a Ce and La atom. During the map acquisition the La atom cannot be seen in the ADF image, probably because it is moving between many stable positions. However, the atom can clearly be seen in the EELS map (g). (h) N and M edges of La (blue) and Ce (green) from this EELS map confirming the atoms are indeed Ce and La. (f-g) have been smoothed.

ing a measurement with small impact parameter and in aloof geometry. This observation is probably explained by delocalization (described in Section 3.2).
 245 That is, even during the period when the atom was away from the electron beam (larger impact parameter) the probability for inelastic scattering (EELS signal) was still high due to delocalization. However, the same is not true for elastic scattering (ADF image). For this reason the atom can be seen in the EELS map but not on the ADF map. This is a fortuitous benefit of delocalization in
 250 spectroscopic measurement.

Finally, this natural atomic movement is a great hindrance for atomically resolved spectroscopy in general. For our EELS experiments, our maximum exposure time has been typically limited by the stability of the atom in the peapod during imaging. Note that the movement is not induced only by the
 255 electron beam and cannot be avoided in this case. For the lanthanide atoms inside peapods this translates to roughly 50 ms or 100 ms per pixel. Still in this time range, atomic jumps were routinely observed. Atomic movement is one of the main limitations for single atom EDX spectroscopy [? ?] (Section 3.4), where exposure times are much longer due to poor collection efficiency.

260 3.4. Single atom X-ray spectroscopy

EDX is a well-adapted tool to study materials containing heavier atoms. The flux of X-ray photons from a given excited atom depends on the fluorescence yield, ω , of a given transition. ω is the ratio of number of X-ray emission events to the number of created core-holes (or vacancies) for a specific tran-
 265 sition. Typically, fluorescence yield measurements are performed using X-ray fluorescence spectroscopy [? ?], where an energy-filtered X-ray source can be used to selectively create core-holes in a shell of the probed atom.

Here we discuss the possibility, that has already been suggested by Lovejoy et al [?], of performing similar measurements in single atoms using EELS
 270 and EDX to probe the excitation and decay events, respectively. One difficulty for such experiment is the choice of the atom to be probed. We have chosen Eu because its $M_{4,5}$ edge occurs around 1100 eV. This energy is sufficiently

high to avoid absorption effects on the vacuum-window of the EDX detector
and sufficiently low to allow EELS measurements (non-negligible inelastic cross
275 section).

In Fig. 5 an experiment at 60 keV with parallel EELS and EDX acquisition
on Eu chains is shown (Fig. 5a-b). The acquisition time to get a statistically
significant EDX signal is about 500 ms, with a probe current of 70 pA (the
current was limited by the requirement to have a sufficiently small probe to dis-
280 tinguish the atoms separated by 3.5 Å). However, even with these long exposure
times 2D mapping of the EDX L and M peaks signal is poor (Fig. 5c-d shows
the integrated Eu M and L signals). An average EDX spectrum on the position
of a single Eu atom (12.5 s acquisition time, marked by a red square in Fig.
5b-d) of the M (Fig. 5e) and the L peaks (Fig. 5f) are shown. A background
285 signal is shown for comparison in green (integrated on the green rectangle in
Fig. 5d). A global average spectrum (198 s acquisition time) of this section of
the Eu chain is shown in Fig. 5g, where the M (α , β and γ) and L (1 , α , β and
 γ) peaks are seen.

Total X-ray emission and absorption events have been measured on a region
290 where a single atom can be identified in the ADF image (red square on Fig.
5(b-d)). The absorption signal has been corrected for the CCD efficiency and
the finite convergence and collection angles. The EDX map shown (5d) does
not allow single atom identification.

The X-ray signal was corrected by a geometric factor due to the detector's
295 solid angle. Moreover, the number of M transitions depends on the number of
 M shell core-holes. After these corrections our measurements are: $EDX_M =$
(550 $\pm$ 90) photons, $EDX_L =$ (700 $\pm$ 100) photons and $EELS_M(100\text{eV}) =$
(1840 $\pm$ 20) M shell core-holes created. Due to the finite energy integration
window (100 eV) the number M shell core-holes created by absorption events
300 has to be corrected. We have estimated the number of missed events using
power laws (this is largest source of uncertainty).

The majority of M shell core-holes are created by the primary electron beam.
These represent direct absorption events, which can be measured from the EELS

Figure 5: (a) Typical ADF image of a Eu atomic chain inside a DWCT. (b-d) ADF image acquired during 2D mapping, EELS Eu M edge map and EDX Eu M peak map. The acquisition time per pixel was 500 ms. (e-f) M and L lines EDX spectrum for one atom integrated on the red square in (b-d). The total integration time was 12.5 s. The background was integrated on the green rectangle, with the same total exposure. (g) Global EDX spectrum (198 s integration time) showing the Eu M and L peaks. Cu from the sample grid and Si from the detector can also be seen. (b-d) have been smoothed. Not all lines are identified in the spectra.

signal. However, L transitions (radiative and non-radiative) also create M shell
 305 core-holes[?]. These have been estimated using the L peak X-ray intensity and
 calculations for the average Auger (a_L) and fluorescence yield (ω_L) coefficients
 for the L peak (4000 extra core-holes). Coster-Kronig M sub-shell transitions
 were not considered, as the signal from all the M transitions has been integrated.

With all these correction the number of core-holes lie in the range $EELS_M(all) =$
 310 [14100; 24400]. The lower bound comes from an E^{-3} and the upper bound from
 an E^{-2} fit to the Eu EELS M edge. With these numbers the estimated fluo-
 rescence yield lies between 0.02 and 0.03 (the theoretical value is 0.0136 ref. [?
 ]). The large uncertainty stems from the necessity to extrapolate the tail of the
 EELS M edge.

315 Our results indicate that 2D mapping of the EDX signal in parallel to EELS
 acquisition from single atoms can be envisaged with an increase in the current
 density (a decrease from 0.35 nm to 0.1 nm translates to approximately ten
 times larger current density) and a decrease in the electron beam energy to 30
 keV (increase in absorption cross section).

320 One of the greatest limitation for these experiments is atomic movement. As
 described in Section 3.3 this limits the exposure time in peapods experiments
 to times of the order of 100 ms. For the Eu chains, in ideal situations, this time
 can be extended to up to 500 ms. This happens because relative movements
 between atoms are less probable in the chains (there is less free space).

325 4. Conclusion

We have demonstrated the current possibilities for single atom detection and
 mapping using EELS and EDX spectroscopies in metallofullerenes and atomic
 chains confined inside carbon nanotubes. The benefits of lowering the energy
 of the electron beam from 60 keV to 30 keV have been explored. Moreover,
 330 the effects of the energy loss, ΔE , at two different acceleration voltages has
 been analyzed. The influence of the motion of atoms inside fullerenes has been
 considered. This motion, which can be induced by the electron beam, greatly

limits the maximum exposure time used in 2D mapping. Finally, we have measured the X-ray fluorescence yield of the Eu M edge by measuring in parallel
335 the absorption and fluorescence signals from individual Eu atoms using EELS and EDX. We concluded that the determination of this quantity is hindered by the large uncertainty in the estimation of the absorption tail in the EELS signal. Also, natural atomic movements are identified as one of the major difficulties in single atom EDX identification.

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References

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