Endohedral fullerenes: a concurrent characterization by means of synchrotron radiation X-ray and IR spectroscopy

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Abstract. Endohedral Metal Fullerenes exhibit a great variety of physical and chemical properties depending on the metal inserted into the cage. These systems are molecular conductors, magnets, ferroelectrics and also superconductors representing extremely promising materials for advanced technologies such as nano-medicine. Here we present temperature-dependent XANES and FTIR investigations of two La@C82 EMF isomers. The combinatorial investigation shows that guest ions move inside the cage perturbing the vibrational states of the carbon cage due to the charge transfer dynamics. Moreover, the principal component analysis points out a discrepancy between temperature-dependent FTIR and XANES based on the occurrence of a non-equilibrium process between charge transfer and cage dynamics. We propose to perform simultaneous time-resolved X-ray and infrared spectroscopy studies to resolve the complex interplay among charge, structure and electric properties of these systems.

1. Introduction

The metal endohedral fullerenes (EMFs) are carbon cluster compounds containing one or more metal atoms inside the fullerene cage [1]. The unique structure of EMFs and their great variety of physical and chemical properties due to the metal inserted in the cage is of great interest. Indeed, EMFs can be molecular conductors, magnets or ferroelectric materials, and can be applied in radiotherapy, in tomography and as contrast agents in medicine and in many other advanced technologies. [2,3] For this reason EMFs have been widely investigated [4,5] in particular, to characterize their unique electronic and structural properties. Among the earliest synthesized EMFs [6], La@C82 certainly represents a prototypical species useful to describe their physical-chemical
properties. It has nine isomers but only two of them can be easily synthesized in a reasonable amount to be measured. As it is shown in Figure 1, C2v and Cs isomers have a different symmetry or structure and, despite of the many investigations, the interplay between their charge and metal dynamics is still not known. Usually, lanthanide metals contribute to the carbon cage with three valence electrons [7,8] forming the electrical structure: M3+C823-. Many different physical pictures have been introduced to properly describe the structural model of an EMF system, but none is fully adequate to describe experimental observations.

The X-ray absorption spectroscopy is a local symmetry-sensitive and element-specific probe. However, it is not easy to obtain structural information by looking at the carbon K-edge due to the multiple occupation sites of carbon atoms in the fulleride structure. To obtain structural information is better looking at the absorption edge of the metal guest and, in order to achieve more accurate structural information regarding the relative position of metal ions inside the carbon cage, theoretical simulations can be combined with X-ray absorption spectroscopy [9]. The Fourier Transform infrared spectroscopy (FTIR) is a vibrational technique based on the absorption of infrared radiation by infrared active molecules that absorb energies within the mid-IR region of the electromagnetic spectrum. In this region we mainly probe two types of molecular vibrations: stretching and bending, typically observed in the wavenumber range ~500–4000 cm–1 (i.e., from 2.5 to ~20 μm). They can be used to retrieve dynamic information in molecular systems as well as solid systems [10].

In the last decade, to extract information not achievable by individual techniques performed independently, the combinatorial investigation of complex systems has been continuously expanding. To characterize the complex dynamics of metal endohedral fullerenes as well as to exploit the advantages of the combinatorial approach, we investigated La@C82 isomers performing both temperature-dependent XAS and FTIR experiments.

2. Experiment and data processing

Detailed information about the sample preparation is available elsewhere [9,11]. Temperature dependent X-ray Absorption Spectroscopy (T-XAS) experiments of La@C82 at the La L3-edge for both C2v and Cs isomers, were performed in the transmission mode at the XAFS station of the 1W1B beamline at the Beijing Synchrotron Radiation Facility, using a Si (111) double crystal monochromator. During experimental runs the storage ring operated at the energy of 2.2 GeV, with an electron current decreasing from 120 to 80 mA within approximately 12 hours. The incident and transmitted beam intensities were monitored using two ionization chambers supplied by a continuous flow of nitrogen gas. A partial suppression of high order harmonics has been achieved by detuning the monochromator crystals by 40%. Experiments were performed in vacuum (~3×10-3 torr) in the
temperature range 35-300 K. Samples were encapsulated in a hole of diameter 1.5 mm, manufactured at the centre of an aluminium holder.

FTIR experiments were performed using the IR synchrotron radiation source of the DAΦNE storage ring: the SINBAD beam line of the Frascati National Laboratory (LNF) of the INFN. Due to the high circulating electron current (> 2 A) of this low energy (E=0.51 GeV) ring, this beamline represents an almost unique IR source in the mid- and far-IR range. Samples were prepared evaporating a liquid droplet casted on a CVD diamond substrate at room temperature inside a glove box fluxed with high purity N2. Using a Bruker Equinox 55 interferometer and a Hyperion 3000 microscope, mid-IR spectra of metal-doped fullerences were collected in the range 600-4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Experiments were performed on samples loaded in the ARS Helitran LT-3He flowing cryostat with a KBr beam splitter using a single element MCT IR detector of area 1 mm\(^2\). The difference among temperature dependent XAS spectra at the La L3 edge were obtained using IFEFFIT \[12\] and SIXPACK \[13\] packages. All spectra were normalized and background subtracted. The IFEFFIT package was used for conventional data pre-processing while the SIXPACK package for the principal component analysis. IR data were subjected to a polynomial background removal and a peak height normalization using the Bruker-OPU\textsuperscript{TM}. In order to extract spectral information, difference spectra were obtained by subtracting the corresponding FTIR or XAS spectra at room temperature.

3. Results and discussions

3.1 Temperature dependent X-ray absorption spectroscopy

Due to their different site symmetry and local structure (Figure 1), temperature dependent XAS spectra of the two isomers, shown in Figure 2, are different. The La L3 edge difference of T-XAS of the La@C82 C\textsubscript{2}v isomer (top panel) exhibits large spectral variations in the region 5475-5525 eV.

![Figure 2](image_url): Comparison of La L\(_3\) edge T-XAS spectra vs. temperature of both La@C82 isomers.

This energy range around the La absorption edge at \(\sim 5483.5\) eV probes the electronic structure (2p-nd transitions) as well as the local geometric configurations around lanthanum metal ions.

Actually, increasing the temperature field both the metal and the carbon atoms of the cage are excited; therefore, the system will experience multiple kinetic states. At low temperature, configurations deviating from the room temperature phase occur around 45 K and 60 K for the C\textsubscript{2}v
and the Cs isomer, respectively. However, for the high symmetry C2v structure, excluding an anomaly at ~45 K the spectral variation is relatively small. On the contrary, the low symmetry Cs structure exhibits large spectral variations at low temperature. As predicted from theory [14], lanthanum atoms move more than 1 Å from its initial position at room temperature. These experiments clearly point out that a large displacement of the lanthanum atom occurs inside the cage also at low temperature and, the motion is really large for the low symmetry isomer. In a previous research, the oscillations of a gadolinium ion inside the carbon cage around the equilibrium position have been described [9]. Actually, with its larger ionic radii, lanthanum ions have a larger amplitude of oscillation than gadolinium.

In order to interpret XANES spectra, we performed theoretical calculations for the optimized structures of the two La@C82 isomers. Figure 3 shows the projected density of states as well as the theoretical La L3 edge absorption spectra (top panels). As discussed in Ref. [9], many equilibrium structures have to be considered and averaged to improve the agreement between theoretical and experimental spectra. To achieve structural information, here we attempted to optimize the metal-fullerene structure neglecting temperature effects but considering the projected density of states. Looking at Figure 3, we may recognize that the local density of La d states of C2v is more structured than Cs. However, the local density of carbon p state is also strongly dependent by the symmetry of the carbon cage. Interestingly, in the XAS spectrum of the C2v isomer the shoulder (at -2 eV) has a La d character while in the Cs isomer the peak at ~5 eV is probably a mixture of La p and d states. The carbon p states distribution is weak and the density of the highest occupied orbital is much larger in the C2v than in the Cs isomer. The local and partial density of states points out that charge transfer effect can be more relevant in the C2v structure.

Figure 3: XANESS spectrum (top) and projected density of states (mid and bottom panels) of the two La@C82 isomers.
3.2 Fourier Transform Infrared Spectroscopy

The mid- and far-infrared spectra of EMFs at room temperature have been studied in details by Lebedkin et al. in Ref. 15. His data show that radial and intermediate vibrations of carbons lie within the range 150-600 cm⁻¹ while longitudinal and lateral vibrations of the metal ion inside the cage and external rotational modes of the molecule fall in the range 40-150 cm⁻¹ and below 50 cm⁻¹, in the far-IR and THz ranges, respectively. Our FTIR data refer only to vibrations in the mid-IR range.

In Figure 4, we compare FTIR spectra of the two isomers in the range 600-4000 cm⁻¹. The marked region (1700-4000 cm⁻¹) is not intrinsic to EMF vibrations and due to hydration. We may identify three characteristic vibrations: the CH stretching mode, the C-C stretching mode and the OH stretching mode. If we consider the average phonon energy of EMFs, this is rather large, i.e., up to 0.2 eV [14] and corresponds to ~1600 cm⁻¹ in wavenumber and ~2300 K in temperature. As a consequence, the temperature field can be considered negligible for the vibrational dynamics of these systems.

In order to correlate the analysis of XAS and FTIR spectra, we performed a principal component analysis (PCA) on both XAS and FTIR datasets. The principal component analysis [17] is a statistical tool aiming at reducing a large dataset to a minimum size, in order to make possible its interpretation. It is widely used in a variety of fields and this approach has been already used for the analysis of XAS spectra in heterogeneous systems [18] as well as to FTIR data. [19] In Figure 5 we present the PCA of temperature-dependent FTIR and XAS spectra of both C2v and Cs isomers of the La@C82. To evaluate the number of major components, we considered the results of two major tools: the scree plot and the cumulative variance. The first gives the eigenvalue representing the weight of the components of the entire dataset while the cumulative variance measures the deviation of the sum of each weighed components with respect to the average data. [17] Together they give the minimum number of components necessary to reconstruct the entire dataset.

For a very large dataset, an indicator function is designed to show the number of major components. In our case, due to the limited size of the dataset, scree plot and cumulative variance
together are sufficient to estimate the major components. In Figure 5 we show how the five T-FTIR spectra of the La@C82:C2v can be reduced to three major components. A similar results is obtained for the T-FTIR dataset of the La@C82:Cs. On the contrary, the analysis of the eight T-XAS spectra of the two isomers returns only two major components. Since FTIR and XAFS datasets were collected independently, the discrepancy points out that FTIR and XAFS techniques are not probing exactly the same sample or, in other words, the same structural configurations as a function of the temperature. It is then impossible to correlate the two datasets in a coherent way. To overcome the drawbacks of collection of experimental data in systems out of equilibrium [20,21] with independent techniques we recently proposed a beamline [22] that combines a synchrotron radiation X-ray and an IR beam into a sub-millimetre spot. This apparatus may perform simultaneous sub-sec time-resolved X-ray absorption spectroscopy and FTIR spectroscopy experiments. It can be envisaged that the capabilities provided by a simultaneous beamline may probe the interplay among electronic, vibrational and geometrical structures in metal endohedral fullerenes and in many other complex systems.

4. Conclusion

We presented an investigation of the dynamics of metal endohedral fullerenes by means of temperature-dependent XAS spectroscopy and FTIR spectroscopy. Changes observed in the temperature-dependent XAS spectra of La@C82 isomers can be associated to the dynamics of guest ions inside the carbon cage, in good agreement with previous theoretical reports. [14] Temperature-dependent FTIR spectra also show different temperature behaviours between the two isomers, characterized by different symmetries as well as different charge transfers. We performed an integral analysis on FTIR and XAS datasets by using the Principal Component Analysis. Datasets collected by different spectroscopic methods at different times show different numbers of major components. The discrepancy does not allow resolving the effective dynamics of these systems, while points out the

Figure.5: PCA of FTIR (top panels) and XAS (bottom panels) spectra of the two La@C82 isomers.
need to perform in these systems simultaneous measurements. In addition to EMFs, many other complex systems and non-equilibrium phenomena can be probed with a simultaneous approach. Moreover, the principal component analysis method can be successfully applied in particular to large datasets collected in a concurrent/simultaneous way on the same sample.

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