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X-ray Raman scattering from the carbon K edge in polymerized C₆₀: experiment and theory

J P Rueff¹, Y Joly², F Bartolomé³, M Krisch¹, J L Hodeau², L Marques⁴,
M Mezouar¹, A Kaprolat¹, M Lorenzen¹ and F Sette¹

¹ European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France

² Laboratoire de Cristallographie CNRS, BP 166, F-38042 Grenoble Cedex 9, France

³ ICMA, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

⁴ Departamento de Física, Universidad de Aveiro, 3800 Aveiro, Portugal

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Abstract

The carbon K near-edge absorption spectra of one- and two-dimensional polymerized C₆₀ have been investigated by non-resonant inelastic scattering in the hard-x-ray regime. The observed changes in the spectra are in good agreement with simulations based on an *ab initio* approach using the finite-difference method, and confirm the [2 + 2] cyclo-addition picture. Our results demonstrate the value of inelastic x-ray scattering as a bulk probe of electronic structure in systems that are difficult to study with conventional x-ray absorption techniques.

1. Introduction

Fullerene molecules, like other non-saturated systems, can polymerize either photochemically [1, 2] or under high pressure (HP) and high temperature (HT) [3]. The polymerization of fullerene molecules has been the subject of numerous theoretical studies within the tight-binding, molecular dynamics, and lately quantum chemical frameworks (see [4] for a review). The covalent bonding between the different C₆₀ molecules is believed to occur through a [2 + 2] cyclo-addition below a critical intermolecular distance estimated to be about 9.2 Å. In this process, two double bonds (one on each monomer) break and reform into a single-bond four-sided ring giving rise to a dumb-bell-like structure. Multiple cyclo-additions on the same monomer will eventually lead to the one-, two-, or three-dimensional polymers. More precisely, in the one-dimensional polymer, the C₆₀ molecules are linked into polymeric chains, while in the two-dimensional polymers they form hexagonal or square polymerized layers [5]. In the three-dimensional polymer, a molecular bonding occurs in the twelve nearest-neighbour directions [6]. The polymerization should modify the electronic configuration of the carbons which participate in the cyclo-addition as well as the local structure around the fourfold C ring. The recent discovery of magnetism in polymeric two-dimensional C₆₀ [7] has further

reinforced the necessity for a better understanding of the electronic properties in this class of materials.

Although a consistent picture can now be derived from theoretical models of the polymerization, no direct experimental investigation of the carbon electronic structure in the fullerene-based polymers has been carried out so far on bulk systems. Soft-x-ray absorption [8] and partial-electron-yield [9] measurements were recorded at the C K edge for polymerized C₆₀. However, these techniques are extremely surface sensitive (in particular, the x-ray attenuation length at the energy of the C K edge is less than 1 μm), which may lead to a misinterpretation of the data, since the fullerene polymers present a large number of dangling bonds at the surface. Furthermore, C₆₀ polymers are prepared under HP/HT conditions and therefore do not possess clean surfaces. This difficulty can be overcome by means of non-resonant inelastic scattering (IXS) in the hard-x-ray regime, where, thanks to the high x-ray penetration depth (of the order of 3 mm in C₆₀ at 10 keV), bulk properties can be probed. In such an experiment, the energy loss spectrum of the scattered photons is measured, following the primary excitation by hard-x-ray photons of typically 10 keV energy, far away from any absorption edges. Consequently, the energy required to excite a core electron is provided by an inelastically scattered x-ray photon. The cross-section for this so-called x-ray Raman scattering (XRS) is given by [10]

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = (e_0 \cdot e_1)^2 r_0^2 \left(\frac{E_1}{E_0} \right) \sum_f \left| \langle f | \sum_{j=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_j} | i \rangle \right|^2 \delta(E - E_{fi}) \quad (1)$$

where r_0 is the classical electron radius. E_0 and E_1 are the incident and scattered energies respectively, E_{fi} is the energy transfer between the ground state $|i\rangle$ and the final state $|f\rangle$, \mathbf{q} is the momentum transfer, and \mathbf{r} is the radial extent of the wavefunction considered. The sums extend over the final states $|f\rangle$ and the coordinates of the electrons j , respectively. Within the dipolar approximation ($q \ll r$), the exponential part of the cross-section can be expanded into $e^{i\mathbf{q} \cdot \mathbf{r}} \approx 1 + i\mathbf{q} \cdot \mathbf{r}$. The matrix element then simplifies to $|\langle f | \mathbf{q} \cdot \mathbf{r} | i \rangle|^2$. If the momentum transfer \mathbf{q} is replaced by the photon polarization vector e_0 , the matrix element is identical to that of the Fermi Golden rule, derived for x-ray absorption [11], and indeed the XRS spectra are identical to the ones recorded by soft-x-ray absorption spectroscopy [10].

In the present paper, we investigate the carbon K edge absorption in different polymerized C₆₀ phases by XRS, both from experimental and theoretical vantage points. The simulations of the observed spectra in the different polymers by an *ab initio* approach validate the picture of the dimerization process through the formation of sp³-type carbon rings.

2. Experimental results

The absorption spectra of the C₆₀ polymers were measured on the inelastic scattering beamlines ID16 and ID28 at ESRF. The detailed set-up of the beamlines has been described elsewhere [12]. The white beam was monochromatized by a Si(111) helium-cooled channel cut yielding a 10 keV beam with an energy width of 1.5 eV. An additional asymmetric Si(400) channel cut was inserted between the monochromator and the spectrometer in order to improve the energy resolution. The scattered photons were energy analysed by a 1 m Rowland circle crystal spectrometer utilizing the Si(555) reflection order close to backscattering, and detected by a Peltier-cooled silicon diode. The total energy resolution was 0.4 eV. The scattered photon energy was kept fixed, while scanning the incident energy, thus varying the energy transfer from 270 to 320 eV through the C K edge. The IXS spectra were recorded at a scattering angle of 10°. This corresponds to $q = 0.88 \text{ \AA}^{-1}$ and $qr \approx 0.17 \ll 1$ for the C 1s wavefunction, a value well within the range of validity of the dipolar approximation.

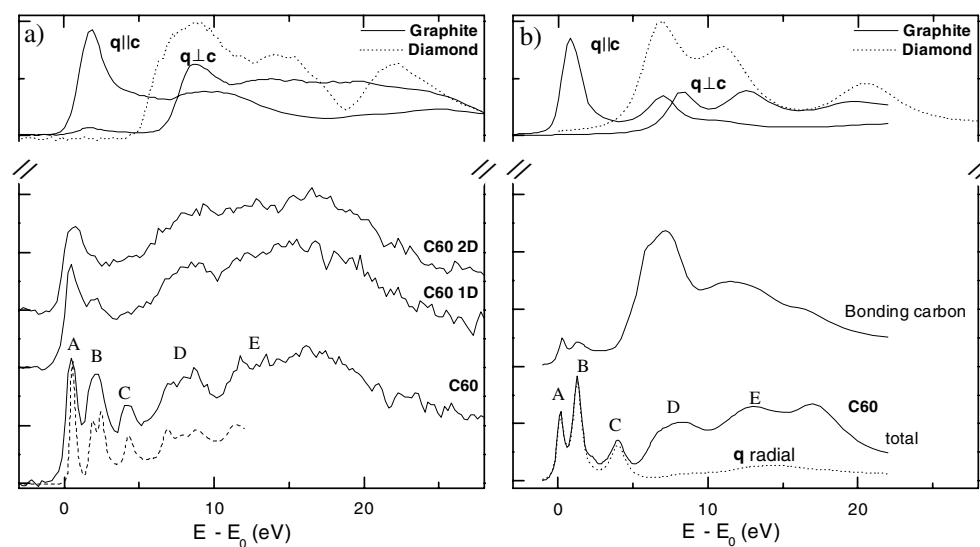


Figure 1. Experimental (left panels) and calculated (right panels) C K edge absorption spectra for polymerized C₆₀ and pure C₆₀, diamond, and graphite as functions of the transfer energy $E - E_0$. The two-dimensional phase was measured in the rhombohedral structure. The C₆₀ soft-x-ray absorption spectrum taken from [14] is also shown (dashed curve). The bonding carbon spectrum corresponds to the isolated contribution from the C* atom in the dimer (see figure 2).

The C K edge absorption spectra were measured in transmission mode in a series of well characterized samples spanning the different ordered C₆₀ polymerized structures. The samples were prepared in the large-volume Paris–Edinburgh pressure cell and recovered upon pressure release as cylindrical pellets with typical diameters of 0.5–1.5 mm [13]. The experimental absorption spectra are displayed in figure 1(a) as functions of the transfer energy $E - E_0$ where E_0 stands for the energy of the elastic peak given by the fixed analyser Bragg angle. The main features are labelled A to E. The absorption spectrum obtained for the pure C₆₀ sample agrees well with the one obtained in the soft-x-ray regime (see figure 1). Large changes in the spectra in the polymerized systems can be noticed particularly in the 0–5 eV region above the edge. The near-edge structure in the pure C₆₀ is characterized by a series of well resolved peaks (labelled A, B, C). These spectral features have been previously attributed to transitions into molecular orbitals of t_{1u} (A), t_{1g} and t_{2u} (B), and a_g (C) symmetry for the leading terms. In the one- and two-dimensional polymers, features A and B have substantially diminished compared to the case for the molecule, and C has almost completely disappeared. At higher energies, two broad and rather featureless structures (D and E), centred at about 9 and 15 eV, can be noted in all the spectra for along the polymer series of approximately the same intensity.

As a first attempt to identify the structures appearing in the absorption spectra in the fullerene-based systems and understand their changes through the C₆₀ polymer series, it might serve to compare those results with the ones obtained on carbon reference samples, where the bonding character of carbon is well characterized. This is the case for the graphite and diamond structures, which represent the archetypal C with sp^2 and sp^3 hybridized bonds, respectively. To this end, the absorption spectra were measured by the XRS technique in graphite and diamond single crystals. The graphite sample was oriented in order to align the momentum transfer q perpendicular and parallel to the c -axis. Thus, depending on the orientation of q , the spectra reflect exclusively either the partial density of states (DOS) of unoccupied π^* - or

σ^* -states for the $q \parallel c$ and $q \perp c$ cases, respectively [15]. In diamond, in the same manner, the measured empty DOS in diamond reflects the σ^* -component. The absorption spectra are shown in figure 1(a). The $q \parallel c$ spectrum in graphite is characterized by a sharp feature peaking at about 2 eV, followed by a broad structure centred at 9 eV, which can be assigned to the empty π^* - and σ^* -states as mentioned above. The weak feature at 2 eV in the $q \perp c$ spectrum may be assigned to tail excitations of the orthogonal component through the finite q -resolution. The absorption spectrum of diamond is closely related to the $q \perp c$ case as expected from the similar symmetry (σ^*) of the probed empty DOS, although the main structure appears broader and is slightly shifted to lower energies.

Preliminary conclusions can be drawn from this comparison: the C_{60} molecule is essentially composed of an sp^2 -carbon network, although the cage bending leads to some admixture of sp^3 character [16]. In the same way, the polymerized structures which have a configuration close to that of the C_{60} molecule contain carbons, in particular those which participate to the bonding between adjacent molecules, with high degrees of hybridization. In a simple picture, one may expect both characters to be identifiable in the absorption edges. In figure 1(a), one may notice that:

- (i) feature D in the absorption spectra coincides with the diamond σ^* -states;
- (ii) the sharp structures at lower energies (A and B) are more closely related to the graphite π^* -states.

The later features are less pronounced in the polymerized systems with the decrease of structure C at higher energies. This simplified picture agrees well with tight-binding calculations which demonstrates that the leading first lowest unoccupied molecular orbitals (LUMO) are π -states [17].

3. Simulations

The absorption spectra were simulated by the FDMNES code using a finite-difference method (FDM) [18]. This method is well adapted to the fullerene-based systems since it allows one to use a non-muffin-tin potential in order to solve the Schrödinger equation. This aspect is a key point when addressing the near-edge absorption fine structure in systems of low symmetry with a hollow structure. This is the case for the C_{60} polymers, where the fullerene cages are distorted because of the intermolecular bonding. It turned out that the inclusion of the core hole in the calculation of the final states is essential, because of the strong excitonic character of the low-energy features [19, 20]. In fact, calculations on non-excited molecules and on an ionized $1+$ molecule including a core hole without a screening effect did not yield a satisfactory agreement between theory and experiment. The best agreement was obtained considering a complete screening of the core hole in the $Z + 1$ approximation where the absorbing carbon atom is equivalent to a nitrogen atom with five valence electrons. With respect to the non-excited molecule this implies a strong loss of symmetry, since only one symmetry plane containing the absorbing atom remains. When the molecule is dimerized, the bonding atom keeps this symmetry plane. Unfortunately, most of the other atoms when excited present no more symmetry operations, and the FDM calculations then become computationally expensive. Calculations neglecting that artificially broken symmetry were unsuccessful as well.

A preliminary computation of the absorption edges was made for graphite and diamond. The results are shown in figure 1(b) for the different polarizations. The calculated spectra have been convoluted with a Lorentzian in order to take into account the core-hole lifetime broadening effect and to remove the occupied DOS. The same procedure has been applied to all the calculated spectra presented in the following. The agreement with the experimental data,

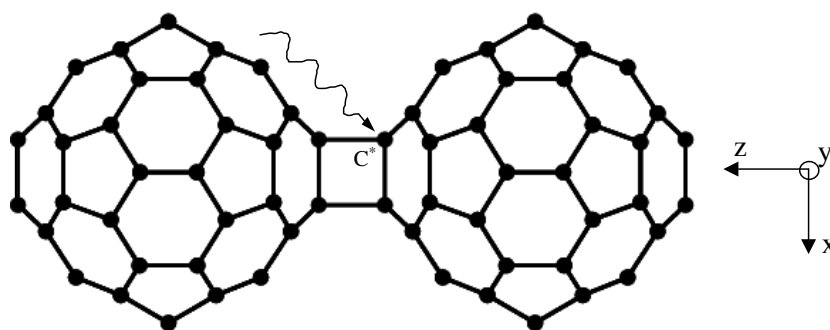


Figure 2. The model (dimer) for calculations of polymerized C₆₀ spectra. The dimer is referenced in the same frame as the C₆₀ molecule. The arrow points to the absorbing atom C* which participates in the inter-cage bonding.

both for graphite and diamond, is fairly good. The separation in energy of the spectral features and their polarization dependence are especially well reproduced, although their amplitude distribution presents some discrepancies with the experimental ones.

The calculation of the C₆₀ molecule is shown in figure 1(b). We used a 4 Å radius cluster, including 18 atoms. Since the 60 atoms of the molecule are equivalent, the choice of the absorbing atom is arbitrary. The calculated spectrum agrees well with the experimental data. In particular, the positions of peaks A, B, and C are well reproduced. Some discrepancies still remain in the relative amplitudes of features A and B, but considering that it is a mono-electronic calculation, and also comparing to the agreements usually reported for other organic compounds, we estimate the quality of the present calculation to be sufficient for further analysis. In order to facilitate comparison to the experiment, a uniform and rigid shift has been applied to all the calculated spectra. Taking this into account, it is noteworthy that the relative edge shift between the calculations on fullerene and graphite is fully consistent with the experimental spectra (the A structure appears at a slightly lower energy for the C₆₀ molecule than the first peak of graphite).

More information can be gained by expanding the calculated spectrum in terms of a projection along the radial direction of the molecule. As can be inferred from figure 1(b), features A, B, and C are essentially due to the radial component. These features are due to transitions to non-localized molecular π^* -orbitals, which project onto the absorbing atoms as a p_z orbital where z is the radial direction, in agreement with molecular orbital calculations [17]. The non-localized aspect of this orbital is revealed by the fact that calculations with smaller cluster radii strongly modify these structures. Transitions to the non-radial components dominate above 5 eV, and are comparable to those in graphite with polarization perpendicular to the c -axis. Thus, we confirm that the C₆₀ electronic structure looks like a distorted graphite electronic structure corresponding to a distorted sp^2 configuration.

To identify the role of the intermolecular bonding in the absorption spectra, the results obtained on the pure C₆₀ molecule have to be compared with calculations on the polymer structures. In order to simulate the absorption in the polymers, a model system consisting of two molecules of C₆₀ (dimer) was used (see figure 2). The distance between the two C dimerized atoms is 1.63 Å, which corresponds to an intermolecular distance of 9.09 Å. The structural parameters were taken from [5]. Note that the structure of each C₆₀ molecule is itself distorted due to the bonding. One especially focuses on the most distorted atom (C*), namely the one making the bond to the adjacent C₆₀ molecule. The four atoms of the first

shell are at a distance ranging between 1.51 and 1.64 Å from this central atom, to be compared to the distances of the three surrounding atoms, 1.40–1.45 Å, in the pure C₆₀ system. The choice of this atom also has the advantage of keeping a symmetry plane which simplifies the computation. The spectrum calculated for this atom with the same 4 Å radius surrounding the cluster is shown in figure 1(b): features A and B are substantially suppressed, and feature C is completely absent. In fact, the general aspect of the spectrum resembles that of diamond, with two peaks at 7 and 12 eV and few non-occupied electronic states at lower energies. We confirm in this way that the atom participating in the dimerization is approaching a sp³ configuration in accordance with the formation of a planar carbon ring predicted in the [2 + 2] cyclo-addition process. Naturally, because the structure is not exactly that of diamond, the electronic structure also retains some aspects of the original C₆₀ molecule.

In order to get the overall spectra of the one- and two-dimensional polymers, one could sum the contribution from all the atoms in each C₆₀ molecule. Because these molecules are distorted, this would require XANES calculations on 15 different atoms which is intractable to process in a reasonable computing time and not so appropriate considering the experimental resolution. Moreover, the most important fact was already emphasized: for hybridization with a neighbouring C₆₀ molecule, the A, B, and C features are strongly reduced in intensity. This is exactly true for the atom making the bond (C*) and must also be partly true for the other atoms because the π*-orbitals are strongly delocalized. Thus, the electronic structure of the non-interconnecting atoms of the buckyball in a polymerized structure will be intermediate between the C* one and that of the original C₆₀. Also, on increasing the weight of the distorted atom compared to the non-distorted one when going from the pure C₆₀ to the one-dimensional (with four bonding carbons) and then to the two-dimensional polymer (with twelve bonding carbons), the amplitude of the A, B, and C features will gradually decrease.

4. Conclusions

In conclusion, the absorption C K edges in pure and polymerized C₆₀ have been determined by XRS. The experimental spectra were successfully simulated with a finite-difference method. The changes in the spectra with the degree of polymerization can be traced back to the cyclo-addition process, thus confirming the previous interpretations [1]. The present work demonstrates that XRS provides a unique spectroscopic tool for investigating bulk electronic properties of light elements in cases where conventional x-ray absorption techniques are very difficult to apply. Potential future applications include the study of systems under extreme conditions (pressure, temperature) and chemically reactive systems, and non-invasive near-edge spectroscopy of geological samples.

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