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**Polarized ATR-IR spectroscopy for the identification of material structure: the case of
graphene oxide**

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ABSTRACT

Graphene oxide (GO) is a layered structure similar to graphite, whose planes of carbon atoms are decorated by oxygen-containing groups. These groups bring hydrophilicity and reactivity to GO, as they are present on its basal plane or at the edges. Thus, their identification is essential to determine the chemical properties of GO. Amongst the possible analytical techniques, infrared spectroscopy is suitable to identify these groups. In this work, an advanced spectroscopic method, polarized attenuated total reflectance infrared spectroscopy, was used to obtain a more in-depth analysis of these reactive groups. This new approach has allowed to refine the description of the functional groups at the surface and could be used to follow the evolution surface processes in material chemistry (e.g. grafting reactions).

Keywords: Spectroscopy ; Thin films ; Carbon materials ; Oxidation

1. Introduction

Graphene oxide (GO) is a 2D material with carbon atomic thickness containing different oxygen functional groups on its surface [1]. The oxygen containing groups are located either at the edges, or on the basal plane of the material where they tend to orient perpendicularly to the GO sheet's plane. The study of the surface composition of GO based on transmission infrared (IR) spectroscopy is tentative as most of the chemical functions absorb in the same wavenumber range. Using an anisotropic film of GO sheets lying down on an ATR crystal [2, 3], proper IR band assignment can be made on basis of the spectroscopic response of GO to a linearly polarized light. Polarized ATR-IR (pATR-IR) spectroscopy has already been used in literature to study several systems including Langmuir-Blodgett films and adsorbed molecules [4-7]. Using pATR-IR on GO will enable to bring insights into the chemical orientation of the different functional groups and to clarify their limitations during chemical reactions, yielding a clearer identification of the reaction sites [8]. This not the case with more sophisticated technique such as XPS, TEM or solid state NMR [9].

In this work, we show the ability of pATR-IR spectroscopy to bring new information on GO surface groups by the analysis of the vibration of several bonds such as C=O, C=C, epoxides and hydroxyls.

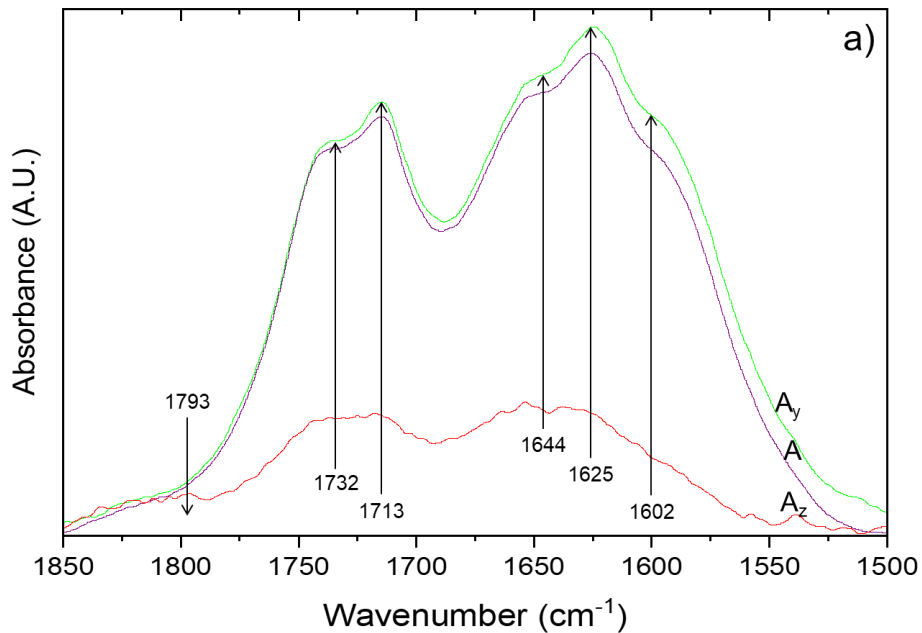
2. Materials and methods

GO was synthesized according to the modified Hummer's method [10] (see SI), and characterized by Raman spectroscopy, XPS and ATR-FTIR (Fig. S1 to S4).

The GO film was prepared by adding on the ATR crystal 1 μ L drop of an aqueous suspension (0.1 g/L) and dried it in the same conditions as for the background spectrum. The operation was repeated 5 times, and the absence of changes in orientation was monitored after each deposit. ATR and baseline corrections were applied. Polarization angle values were 0° (parallel component transmitted, Fig. S5) and 90° (perpendicular component transmitted, Fig. S5). Instrument details can be found in SI.

3. Results and discussion

Two regions have been investigated and interpreted separately. First from 1800 to 1500 cm^{-1} (Figure 1), corresponding the stretching of C=C bonds from the graphitic regions and stretching of C=O bonds. Since the stretching modes belong to the plane of GO, most of the sheets are lying down on the ATR crystal (xOy plane). A_z value in this wavenumber range being non-zero, the sheet's packing order is not perfect. Figure 1a) confirms that the IR active moieties in this region are mainly oriented in the xy plane. Six bands are observed on the unpolarized spectrum. The normalized



polarized spectra (Figure 1b)) show these bands as intense on A_z as on A_y , except at 1602 cm^{-1} .

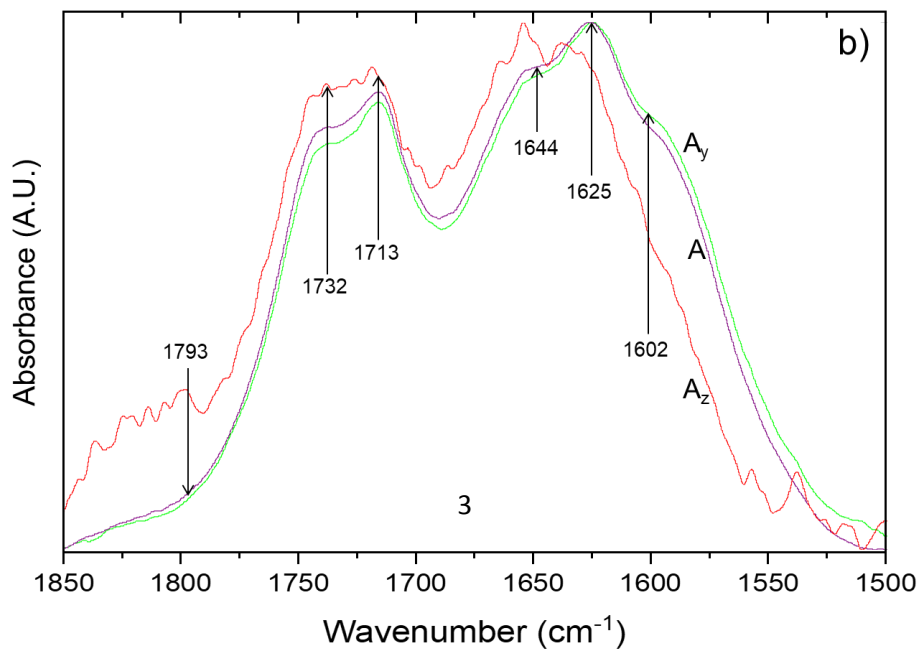


Figure 1. A (purple), A_y (green) et A_z (red) components of a) the raw spectra and b) the normalized spectra of the GO film.

The band cluster centered at 1635 cm^{-1} corresponds to the stretching of the C=C bonds composing the graphitic network [11], hence the 1602 cm^{-1} band is in agreement with its assignment to a C=C bond stretching mostly oriented along the xy plane [12]. The signal found on A_z around 1793 cm^{-1} can be associated to the C=O bond stretching of carboxylic acid groups [12-14] since they are perpendicular to the sheet plane [15] and as 1732 and 1713 cm^{-1} bands are assigned to carbonyls C=O groups [15]. Figure 1b) suggests that this band originates from a low amount of COOH groups in the film instead of a packing defect. According to molecular simulations [15], the shoulder at 1644 cm^{-1} may be assigned to stretching modes of more complex carbonyl-containing groups such as benzoquinone or pyrone. For the signal at ca 1625 cm^{-1} , several assignments were made in literature [12,13,16]. Based on orientation, the 1625 cm^{-1} signal might come from the C=O stretch near a vacancy of the graphitic sheet [17].

The second region of interest is between 1500 and 900 cm^{-1} (Figure 2), which allows to describe the diversity of functional groups in GO. These signals could be assigned to organic SO_4 groups (formed upon oxidation of the graphitic network, Figure S4) [18] and the epoxide asymmetric stretch on the basal plane [19]. The weaker A_z component's band area with respect to A_y (Figure 2a)) suggests that more complex geometric environments are probed.

Three bands are identified in Figure 2. Since graphite oxidation takes place in patches on the graphitic sheet [20], the closeness of the moieties is likely to result in important geometry distortions. Hence, the 1405 cm^{-1} band would be consistent with the bending of basal hydroxyl groups in a distorted environment. The 1378 cm^{-1} signal is associated to the basal OH bending mode while the 1452 cm^{-1} signal may come from the C-O stretching bond of phenolic OH.

In the low wavenumber range, A_y is not perfectly overlapped with the unpolarized spectrum (Figure 2a)), which implies that A_z is participating to the unpolarized spectrum as more than just as a result of packing defects.

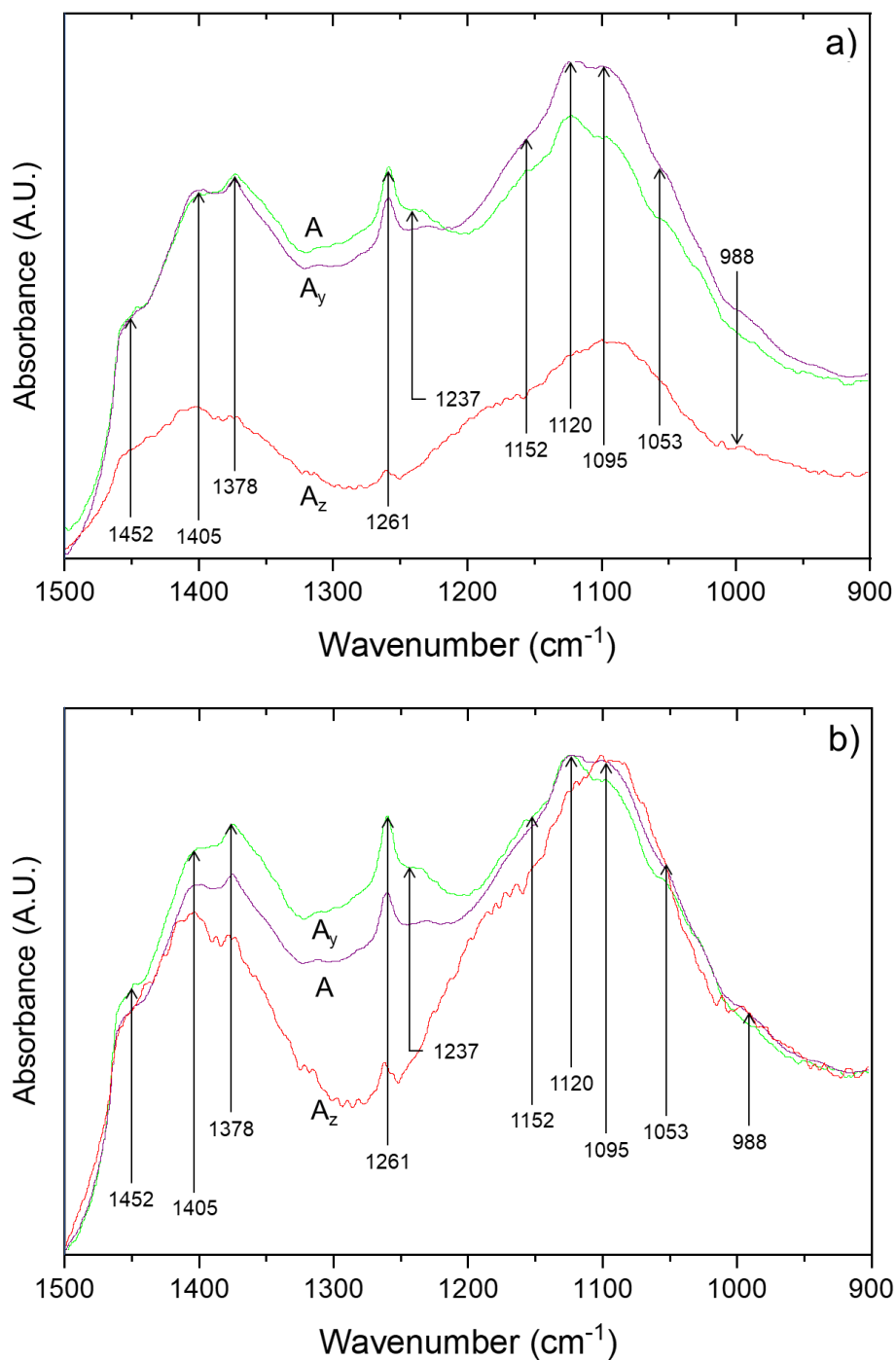
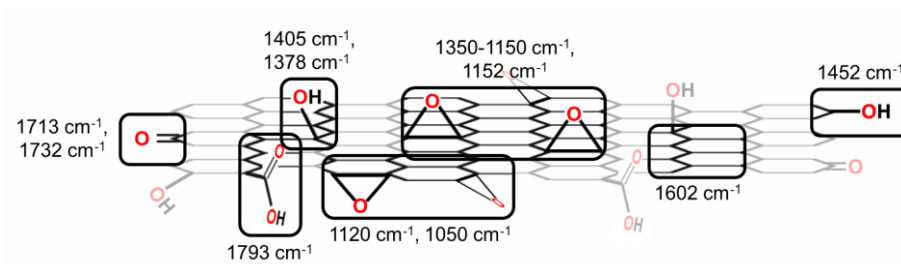


Figure 2. A (purple), A_y (green) and A_z (red) components of a) the raw spectra b) and normalized spectra of the GO deposit in the 1500-900 cm⁻¹ region.

The 1053 cm⁻¹ signal is usually assigned to epoxide groups. It is predominant on A_y, so it can come from edge epoxide groups. The 1120 cm⁻¹ band is more intense on A_y and, on basis of the

assignment of the 1053 cm^{-1} band, it may be associated to the asymmetric stretching mode of edge epoxide groups where the cycle is no longer constrained by the surrounding graphitic moieties. The 1152 cm^{-1} band corresponds to basal epoxide groups symmetric stretching [12]. All new band assignments that have been made in this study are summarized in Table 1 and Figure 3.



Wavenumber (cm^{-1})	Orientation	Assignment	Reference
1793	$\perp \perp$	C=O, carboxylic acid	this work
1713, 1732	//	C=O, carbonyls groups	this work
1644	//	pyrone, benzoquinone	[13], this work
1625	//	C=O, ketone near vacancy	this work
1602	///	C=C, graphitic	[9,10], this work
1452	//	C-O, phenol	this work
1405	//	basal COH bend	[10], this work
1378	//	basal C-O(H)	this work
1350-1150	///	SO_4^{2-} , basal epoxide groups (as)	[14], this work
1152	$\perp \perp$	basal epoxide groups (s)	this work
1120	-	edge epoxide groups (as)	this work
1050	-	edge epoxide groups (s)	this work

4. Conclusion

Polarization ATR-IR spectroscopy enabled to enlighten several points about the characterization of GO by IR spectroscopy. The GO sheets are mainly oriented along the xy plane and

the study of region 1500-1000 cm^{-1} enabled to clarify some of the band assignment with respect to literature. Among other assignments, basal and edges epoxides are distinguished, and carboxylic acids in different environments are found. The present results will be taken further by calculation of polarized spectra from computational methods. Thus, this approach allows to refine the identification of the surface groups and will be useful to follow their evolution during surface processes such as grafting reactions.

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6. References

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