

# Resonant Raman Scattering of Graphite Intercalation Compounds : mono, bi and tri-layer of graphene doped by potassium : $KC_8$ , $KC_{24}$ and $KC_{36}$

Pascal Puech,<sup>1</sup> Yu Wang,<sup>2</sup> Iann Gerber,<sup>3</sup> Alain Pénicaud<sup>2</sup>

<sup>1</sup> CEMES-CNRS, UPR8011 and Université de Toulouse, UPS, F-31055 Toulouse, France

<sup>2</sup> CNRS, CRPP, UPR 8641 and Univ. Bordeaux, F-33600 Pessac, France

<sup>3</sup> Université de Toulouse, INSA-CNRS-UPS, LPCNO, 31077 Toulouse, France  
[pascal.puech@cemes.fr](mailto:pascal.puech@cemes.fr)

Properties of graphite intercalation compounds (GICs) are highly dependent on the number of graphene layers intercalated by atoms or molecules. Stage 1 corresponds to a monolayer surrounded by intercalants, stage 2 (or 3) corresponds to a bilayer (or trilayer) surrounded by intercalants. The charge transfer per carbon atom is characteristic of each intercalant and can be positive (p doping) e.g. with sulfuric acid or negative (n doping) e.g. with potassium. In recent years, there has been a renewed interest in GICs as GICs are considered as a model system for graphene but also a route to synthesize graphenide (negatively charged graphene) solutions.

Raman scattering is a powerful technique which has proven invaluable for characterization of pristine graphene. In the specific case of potassium intercalated compounds, the Raman spectrum under certain excitation energy has been studied by line-shape analysis in order to understand the electron-phonon coupling [1]. Recently, ab initio calculations have explained the observed Raman shifts [2]. So far, resonant Raman scattering of potassium intercalated graphite with different excitation energies is still missing. We will present Raman spectra from UV to infrared and show how the coupling between the light and the electron-phonon mode changes [3]. Potassium is known to give its electron leading to a large charge transfer close to  $-1/8$  for stage 1 ( $KC_8$ ) and  $-1/24$  for stage 2 ( $KC_{24}$ ). The question is more subtle in stage 3 ( $KC_{36}$ ) for which the graphene layers are not equivalent. For stage 3, two Raman G bands are clearly visible, corresponding to the interior layer and the boundary layers, respectively.

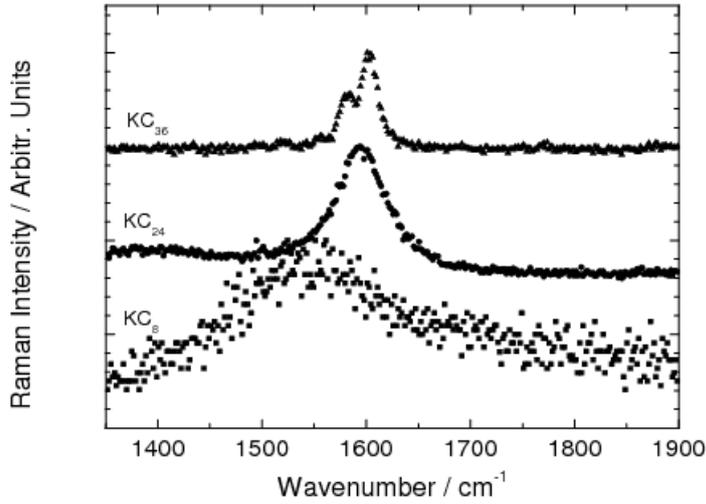
By varying the excitation energy from UV to infrared, we observe that the intensity of the boundary layers G band versus that of the interior layer is maximum at 2.5 eV, leading to a sharp resonance profile at room temperature. Using first principle calculation, we associate this transition to  $\pi$ - $\pi^*$  of the bounding layers. Statistical analysis has been used. We will show that close to the resonance, the fluctuations are huge. Depending to the choice of the plotted quantities (Raman intensity of the boundary layers versus the Raman intensity of the inner layer), we can observe quasi-divergence (our report, see figure 2) or on the contrary (inverse ratio) a nearly zero value masking the phenomenon [4].

[1] J. C. Chacon-Torres, A. Y. Ganin, M. J. Rosseinsky, T. Pichler, Phys. Status Solidi B **249** (2012) 2640.

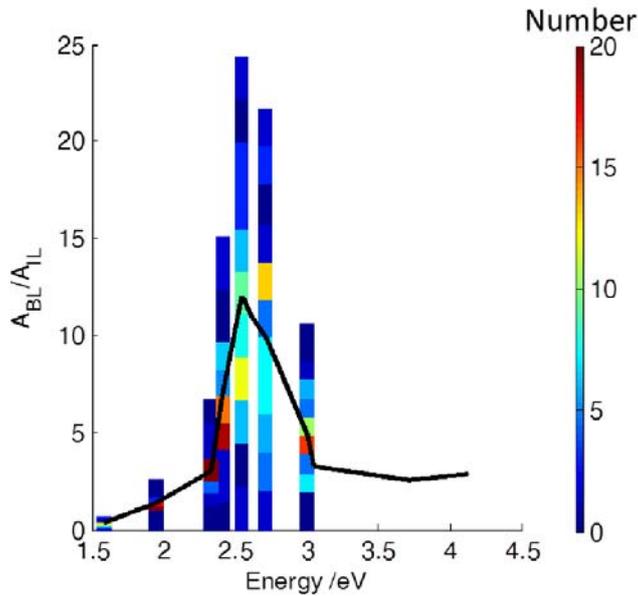
[2] A.M. Saitta, M. Lazzeri, M. Calandra and F. Mauri, Phys. Rev. Lett **100** (2008) 226401.

[3] Y. Wang, P. Puech, I. Gerber and Alain Pénicaud, J. Raman Spec. DOI 10.1002/jrs.4445.

[4] J.C. Chacon-Torres, L. Wirtz, T. Pichler, ACS Nano **7** (2013) 9249.



**Figure 1** : Typical Raman spectra obtained with an excitation energy of 3.71 eV.



**Figure 2** : Ratio of the integrated intensity of the G band for boundary over interior layer (40 to 50 spectra depending on the excitation energy). Color codes for statistics: the number of times the experiment yields the corresponding ratio. The black line corresponds to the average value. It is clearly seen that measurements give very narrow distribution away from the resonance and highly dispersed data near and on the resonance.