Crumpling in multilayer graphene: signature in Raman spectra

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Richness and complexity of Raman spectra related to graphene materials is established from years to decades, with, among others: the well-known G, D, 2D,... bands plus a plethora of weaker bands related to disorder behavior, doping, stress, crystal orientation or stacking information [1]. Herein, we report on how to detect crumpling effects in Raman spectra, using a large variety of few and multilayer graphene [2]. The main finding is that these crumples enhance the G band intensity like it does with twisted bi layer graphene. We updated the D over G band intensity ratio versus G band width plot, which is generally used to disentangle point and linear defects origin, by reporting surface defects created by crumples, introducing '2D defects'. Moreover, we report for the first time on the existence 23 resonant additional bands. These bands are only observed at 633 nm, with a resonance mechanism. Twelve of these twenty-three bands are observed in the range 600-1600 cm^{-1}. The eleven other bands are observed at higher wavenumber, and are interpreted as second harmonic or a combination of the twelve wavenumbers cited previously. Their attribution will be discussed in light of recent GERS (Graphene Ehanced Raman Spectroscopy) literature. We use Raman plots (2D bands versus G band positions and widths) to gain qualitative information about the way layers are stacked [3]. For some samples, we also report on the Raman behavior of low frequency shear and layer breathing modes.

[1] A. Merlen, J. G. Buijnsters and C. Pardanaud, *Coatings 2017, 7,* 153

[2] D. Nikolaievskyi, M. Torregrosa, A. Merlen, S. Clair, O. Chuzel, J. L. Parrain, T. Neisus, A. Campos, M. Cabie, C. Martin, C. Pardanaud, *Carbon* 2023, 203, 650

[3] C. Pardanaud, A. Merlen, K. Gratzer, O. Chuzel, D. Nikolaievskyi, L. Patrone, S. Clair, R. Ramirez Jimenez, A. de Andrés, P. Roubin, et al., *J. Phys. Chem. Lett.* 2019, 10, 3571