

FIG. 1. Background-subtracted spectrum (black dots) of sample D at the first pressure point is plotted over the 2D range. The optimum fit to two Lorentzians is shown as blue lines. The narrow peak corresponds to the second-order Raman from the diamond anvil.

### RAMAN SPECTROSCOPY UNDER HIGH PRESSURE

To apply high pressure, we loaded the samples into a membrane diamond anvil cell with anvils of 500  $\mu\text{m}$  culet size and Type IIa diamonds. The intense Raman peak of the diamonds overlap with the D band of graphene. Both shift with pressure and therefore not much reliable information of the D band could be obtained. The ruby luminescence R1 line was used for pressure calibration.[1] DMF and PMMA are not common pressure transmitting media (PTM) in high pressure experiments as the hydrostaticity is not guaranteed. We loaded 3 ruby pieces into the cell in different locations to monitor the hydrostaticity at high pressure. The full width at half maximum (FWHM) of the GM Raman peaks of graphene, plotted with pressure in the supporting information (SI), can be used as an additional indication of hydrostaticity. We stopped increasing the pressure when a large non-hydrostaticity was observed at 5 GPa for sample P and 7 GPa for sample D.

We performed non-polarized Raman measurements in the backscattering geometry with a Horiba T64000 Raman system with a confocal microscope, a single 1800 grooves/mm grating, a 100  $\mu\text{m}$  slit and a liquid N<sub>2</sub>-cooled CCD detector (Jobin-Yvon Symphony). For both samples, the highest signal to noise ratio of the Raman signal is obtained at 514 nm excitation, compared to 488 and 647 nm, at the same spectra-collecting condition. An edge filter for the 514 nm line from a Coherent Innova Spectrum 70C Ar<sup>+</sup>-Kr<sup>+</sup> laser was used. We kept the laser power on the sample below 5 mW to avoid significant laser-heating effects on the graphene and the concomitant softening of the Raman peaks.

### EVIDENCE OF UNSUPPORTED MONOLAYER GRAPHENE

An increasing number of peaks (therefore fitting parameters) usually brings the fit closer to the data. The Bayesian information criterion (BIC) gives a penalty to introducing additional fitting parameters to avoid over-fitting. We present the best fit of the spectrum of sample D at the first pressure point over the 2D range after subtracting the background using a 5-term polynomial in Fig. 1. The fit consists of two Lorentzians — the left from the diamond and the other from graphene. Increasing the number of peaks or changing the shape of the peaks increases the BIC, and is therefore a less good fit to the data. We reasonably conclude that the interaction between the graphene pieces in sample D is too weak to form multilayer graphene from the objectively fitted single 2D peak. The fitted peak width is about 31 cm<sup>-1</sup>, which is a typical value of monolayer graphene [2].

We also present the evolution of the GM width with increasing pressure in Fig. 2. The width of the GM can be affected by many factors. vdW between graphene and a substrate can broaden a Raman peak. With contact to condensed matter on both sides in this work, a factor of 2 broadening seems reasonable. In fact, it is normal that the width of the GM of CVD graphene on Cu [3, 4] is twice that of high quality exfoliated monolayer graphene on h-BN [5]. Also, this figure shows no consistent broadening (if not narrowing) of the GM with pressure in the pressure range of interest. Lack of features related to the separation of two or more components of the G and 2D bands at ambient condition or under pressure is compatible with the claim that the graphene samples used in this work is of monolayer in liquid and solid DMF [6].

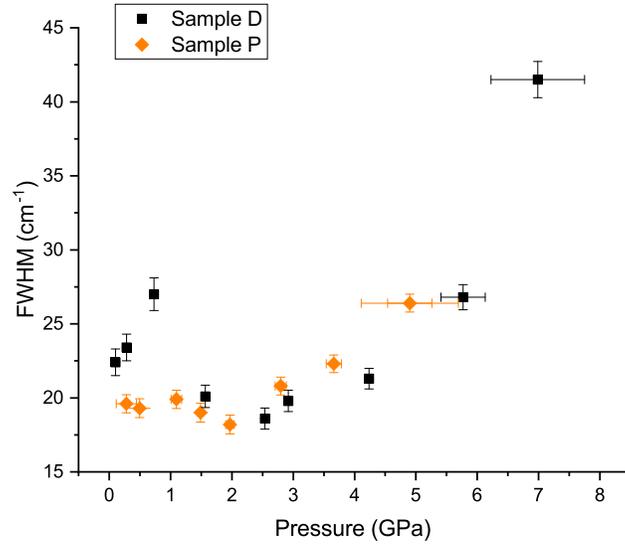


FIG. 2. The FWHM of the GM of the samples D and P is plotted versus pressure. The uncertainty in both pressure and width is plotted where it exceeds the size of a data point.

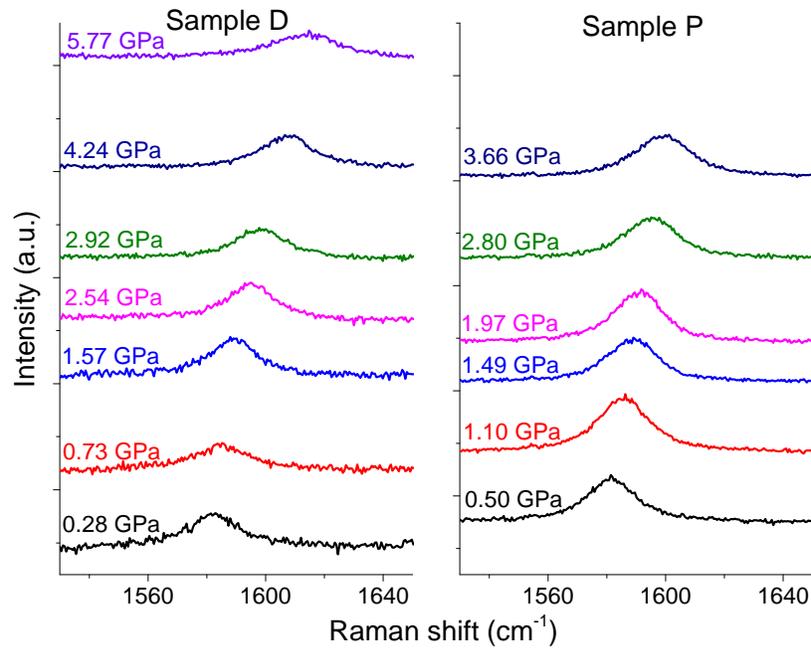


FIG. 3. The spectra of the samples D and P over the GM range are presented. The spectra are vertically shifted proportional to pressure. We fit each spectrum by a single Lorentzian to obtain the GM frequency plotted in Fig. 2 in the main text.

## DATA

We finally present the spectra under pressure in Fig. 3.

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