Operation of graphene-on-quartz acoustic cavity at cryogenic temperatures

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This paper presents observation of mechanical effects of a graphene monolayer deposited on a quartz substrate designed to operate as an extremely low-loss acoustic cavity standard at liquid-helium temperature. Resonances of this state-of-the-art cavity are used to probe the mechanical loss of the graphene film, assessed to be about $80 \times 10^{-4}$ at 4K. Significant frequency shifts of positive and negative sign have been observed for many overtones of three modes of vibration. These shifts cannot be predicted by the mass-loading model widely used in the Quartz Microbalance community. Although thermo-mechanical stresses are expected in such a graphene-on-quartz composite device at low temperature due to a mismatch of expansion coefficients of both materials, it cannot fully recover the mismatch of the mass loading effect. Based on a force-frequency theory applied to the three thickness modes, to reconcile the experimental results, the mean stresses in the graphene monolayer should be of the order of 140 GPa, likely close to its tensile strength.

I. INTRODUCTION

Bulk acoustic wave (BAW) devices are widely used in research and industry as resonators/cavities, filters or sensors, including Quartz Crystal Microbalance (QCM) 1,2, for a large variety of applications. Beyond these usual applications at room temperature, it has been demonstrated that plano-convex BAW cavities made of premium-quality quartz and designed to trap the acoustic energy can exhibit Quality factors greater than a billion in the frequency range 1 – 200 MHz at liquid helium temperature 3,4. In these conditions they become very attractive for various experiments in fundamental physics 5,7 as well as for hybrid quantum systems 8, optomechanics 9,11, etc. With that in mind, the BAW device described in this paper has already been operated as an optical cavity 12. Consequently, the ability of these devices to be simultaneously both an acoustic and an optical cavity makes them a natural candidate for optomechanical experiments. Although, the material based interaction strength between optical and acoustic fields within the same volume of the cavity remains low. In addition to coupling in bulk, one can be enhanced on a boundary by depositing a mirror coating. On the other hand, it has been demonstrated 13 that deposition of traditional metallic coatings like chromium and gold leads to significant degradation of acoustic Quality factors. This motivates investigations of effects of ultra thin graphene layers on BAW devices with a promise of minimizing the loading impact on mechanical losses (i.e. without reducing Q-factors) 14,15. In this work, we present the first tests of BAW cavities with graphene coatings.

The device under test, a BAW cavity, is an electrodeless version of a premium-quality quartz crystal resonator as shown in Fig. 1. The crystal is a doubly rotated SC-cut (Stress Compensated corresponding to rotation angles $\phi = 22.4^\circ$, $\theta = 34.0^\circ$) exhibiting a low stress-to-frequency sensitivity of its metrologic mode, the slow thickness shear or C mode. It is 1 mm thick at its center, and its diameter is 15 mm. With these dimensions the device exhibits a 3rd overtone (OT) of this mode at 4.99 MHz. Vibration frequencies of the 3rd OTs of the fast thickness-shear mode, the B-mode, and the longitudinal thickness mode, the A-mode, are located at 5.47 MHz and 9.31 MHz respectively. Typically all these odd OTs could be excited piezoelectrically with electrodes deposited on a supported structure (Fig. 1). The resonator plate itself is a plano-convex lens and both electrode supports are also shaped accordingly in order to trap the vibration at the center of the active disk. This specific device can be dismantled rather easily to coat one or both surfaces of the vibrating plate.

The characterisation of graphene coating effects was made in two steps. Firstly, the DUT was measured in its nominal configuration (no electrodes) at room temperature (RT) and at 4K. Secondly, the BAW cavity was characterised with the graphene layer 5 mm in diameter put on a single face. This layer 16 was grown on copper foils by the Chemical Vapor Deposition (CVD) method and then transferred to the quartz surface by the manufacturer according to a standard transfer process. The provider specifies that the monolayer is typically 0.35 nm thick 17 with grain size up to 10 nm. Additionally, As a reference test, the same BAW devices had been used with gold and chromium coatings on both sides successively in order to compare their respective effects on the resonator behavior 13. The device before and after the graphene coating is characterised in terms of resonance frequencies and corresponding Quality factors (inverse of mechanical
losses) according to a well-defined procedure \[13\]. The method is based on measuring equivalent electrical parameters of the device with a network analyzer locked on a Hydrogen maser while the device is in a commercial pulse tube cryorefrigerator.

II. GRAPHENE MECHANICAL LOSS AT 4K

Low loss acoustic cavities can be used to probe mechanical losses in various coatings [13]. Indeed, total losses of a coated device is a sum of intrinsic losses of the acoustic plate and the coating material. So, by comparing Quality factors of these devices before and after coating, one can deduce material properties of the added layer. Thus, since the BAW resonator internal losses set limits on the detectable effects, it is straightforward to discuss the main dissipation mechanisms limiting BAW performance. For frequencies typically greater than a few Megahertz and at room temperatures, BAW devices operate in the Landau-Rumer regime [19], because the thermal phonon lifetime is \(1/\tau_{th} < f < k_BT/\hbar\). In this regime the acoustic wave absorption coefficient \(\alpha(f)\) is proportional to \(T^n f\) with \(n\) close to 4 or 6 depending on whether the acoustic wave is a shear one or longitudinal [19] [20]. Consequently, the \(Q\)-factor becomes independent of the frequency [21] because \(Q \propto \frac{f}{\alpha(f)}\) where \(V\) is the wave velocity. Although these relationships are true for intrinsic losses linked to a three phonon mechanism, in practice, additional engineering losses may lead to deviations from this law for lower frequencies and surface scattering may result in \(Q\) degradation for higher frequency ranges. Moreover, at lower temperatures a BAW device performance may be also limited due to Two Level System absorption [21][22].

Additional loss of a deposited layer, e.g., graphene, can be estimated from the Young moduli [23] of both the substrate, in this case crystalline quartz, and the coating [13]. For further analysis, anisotropy of quartz as well as its weak piezoelectric effect are neglected. Assuming that intrinsic losses in both layers are dominant and that the interface damping is negligible, resulting losses in the coated device can be simplified as:

\[
\phi_{\text{coated}} = \phi_q + \frac{\xi_g}{\xi_q} \phi_g \approx \frac{\xi_g}{\xi_q} \phi_g \approx \frac{3m_g V_t}{t_q Y_g} \phi_g, \tag{1}
\]

where \(\phi\) denotes mechanical loss (\(\sim 1/Q\)), \(\xi_g (\xi_q)\) is the energy stored in graphene (quartz), \(Y_g (Y_q)\) is Young’s moduli, and \(t_q\) the thicknesses. The graphene Young modulus along the layer plane of 1TPa has been previously measured at room temperature [24]. That of quartz is estimated to be 66GPa [13]. From experimental data plotted in Fig. 2, a 1mm thick quartz coated with a 0.35nm thick layer of graphene exhibits mechanical losses \(\phi_{\text{coated}} \approx 10^{-7}\). Thus, the graphene layer loss at 4K can then be estimated from Eq. (1) as close to \(\phi_g \approx 80 \times 10^{-4}\) with an uncertainty mainly linked to that of the Young modulus of a graphene monolayer at 4K. Similar values have been observed for gold and chromium coatings under the same operating conditions: \(\phi_{Au} \approx 4 \times 10^{-4}\), and \(\phi_{Cr} \approx 16 \times 10^{-4}\) respectively with the latter depending on frequency \[13\].

Dependence of \(Q\)-factors on temperature shown in Fig. 3 suggests that losses for \(T > 4K\) are limited by phonon-phonon interactions corresponding to the Landau-Rumer regime, because \(Q\)-factors scale as \(T^{-n}\). Since intrinsic loss still dominate engineering loss, the DUT can be considered as high quality in terms of energy trapping, defects and surface quality. Nevertheless, the exponent \(n\) is less than 4 instead of typically \(4 \leq n \leq 6\) [20][25]. For lower temperatures, a \(T^{-7}\) scaling law could be attributed to residual impurities in the synthetic quartz crystal generating TLS [3][26].
III. STRESS INDUCED FREQUENCY SHIFTS

In addition to the Q-factor measurements, effects of the coating can be also characterised by the corresponding frequency shifts. For experimental investigation of such frequency shifts at room temperature, the 3rd OT of the C-mode was chosen since it exhibits a rather weak temperature sensitivity which is close to $+4 \times 10^{-8}$ K$^{-1}$ at 300K. In contrast, both the B-mode and A-mode are very temperature sensitive (typically more than $-5 \times 10^{-5}$ K$^{-1}$ at 300K for the B-mode 3rd OT). However, at 4K, fractional frequency sensitivity to temperature changes for all modes and OTs is typically limited to a few $10^{-9}$K$^{-1}$. So, at these temperatures all acoustic modes may be employed to compare frequencies before and after graphene coating.

The simplest mechanism behind the frequency shift is called the mass loading (ML) effect: adding an extra layer of material increases the effective mass of acoustic modes leading to decrease in frequency which is inversely proportional to the mass. This effect is commonly used to tune the resonance frequency of electroded devices. It is important to note that the graphene layer cannot resonate by itself because its thickness is much lower than half of the acoustic wavelengths concerned in this work. Frequency shift of an acoustic mode resonating at $f_{n0}$ due to this effect can be estimated as:

$$\frac{\Delta f_n}{f_{n0}} \approx -\frac{\rho_q t_q}{\rho_l t_l},$$

where $\rho_q$ ($\rho_l$) is mass density of quartz (layer), $t_q$ ($t_l$) is thickness of quartz (layer). This shift does not depend anymore on the vibrating mode type, A, B or C, at the first order (See Appendix A). This estimation approach has become popular in the QCM community, and known as Sauerbrey formula [27][33].

For the room temperature demonstration, frequencies of the C-mode 3rd OT have been compared before and after graphene coating at room temperatures revealing a negative fractional frequency shift $\Delta f/ f_{300} \approx -8 \times 10^{-7}$. The sign of this shift agrees with the mass-loading effect. Although, by using Eq. (2), the measured frequency shift would suggest an additional areal mass of 21ng/mm$^2$ which is much more than expected. Indeed, with a graphene thickness of the order of 0.35nm and a quartz thickness of 1mm Eq. (2) gives $\Delta f/ f_{300} \approx -3 \times 10^{-7}$. Realistically such a discrepancy could be attributed to contamination [17, 34] and/or some kinds of coating defects such as buckles or wrinkles for example [35, 36] as well as strains occurring by either stretching or compressing the graphene layer during its transfer process [37]. The mass density of a thin film of graphene could also be discussed in comparison with that of the corresponding bulk material [35], but that does not change the result dramatically. To find the actual explanation for the observed deviation, tests at low temperatures have been preferred.

A relative frequency shift between the uncoated and graphene-coated resonator at 4K can be calculated based on frequency shifts at 300K and integrated coefficients of thermal expansion (ICTE) from 300K down to 4K. As a result, the fractional frequency shift at 4K, would be that at 300K multiplied by $+0.9936$ or $+0.9885$ depending on the reference source of graphene CTE, that is $-3 \times 10^{-7}$. These calculations of the mass loading effect have been validated by applying them to more usual gold and chromium coatings and consolidated by experiments at 4K, giving measured fractional frequency shifts in good agreement with those expected from mass loading (see Appendix A). Although the methodology works,
the mass loading model does not hold anymore in the case of a graphene coating. The measurements of frequency deviations of coated and uncoated crystals made at 4K are plotted in Fig. 3. Here, contrary to the mass-loading model, both shear modes exhibit a positive frequency shift proportional to the overtone number \( n \). Although, the longitudinal mode demonstrates the frequency shift expected from mass loading, i.e. a negative slope proportional to \( n \), the slope itself significantly deviates from the expected mass ratio of graphene coating and quartz.

To improve the mass loading model, one may add viscoelasticity of the coated film. This involves the ratio of Young modulus weighted by their respective densities \([32, 33]\). Although the corresponding correction term remains negligible. Additionally, some other typical QCM modifications in a small load approximation have also been considered, keeping in mind that adhesion of graphene is strong \([39–41]\). Among them friction mod-
ifications could explain a positive slope of frequency shifts for both the C and B modes. In the same time analytical formulas can also be used coming from constrained contractions of its four bridges induced by cooling from RT to 4K. Assuming that the resonator rim is clamped, the naked device would exhibit a fractional frequency change \( \Delta f/k \) from the ideal reference state at 4K of \(-0.32 \times 10^{-3}\) for the A-mode, \(-0.18 \times 10^{-3}\) for the B-mode, and \(+1.86 \times 10^{-5}\) for the C-mode.

A more realistic additional effect that could, at least partially, improve predictions of the model is static thermomechanical stresses which definitely exist in this composite device due to a mismatch of graphene and quartz thermal expansion coefficients. Indeed, tests are performed at cryogenic temperatures while the graphene coating on the quartz substrate was deposited at RT according to a nominally stress-free process. Graphene exhibits a negative thermal expansion coefficient \([46]\) whereas that of quartz along the x-axis is always positive \([46]\), and that along the z-axis becomes negative between 5 and 12K. Due to this mismatch, the quartz plate bends because the graphene film is coated only on one side. The associated stress gives frequency shifts that are consistent with our experiment data (Fig. 1) and supported by other arguments. Firstly, works by Ballato, Eernisse, and others show that stress induced frequency shifts are proportional to the operating frequency. Secondly, theoretically the A-mode shifts happen in opposite sign when compared with C and B mode deviations with respect to azimuth angle \([47]\). Thirdly, C-mode frequency shift observed experimentally is much lower in absolute values than that for the A mode since the SC-cut plate is optimized to exhibit low stress sensitivity of the C-mode at RT.

Effects of a static mechanical bias on elastic waves, i.e. small dynamic fields superimposed on a static bias, were intensively studied in 70’s-80’s \([48–51]\) after Thurston and Brugger works in 1964 \([52]\). In this work, we employ Sinha-Tiersten’s perturbation analysis limited to the perturbation of the elastic constants and not including dielectric or piezoelectric constant changes for example which can be justified by the weak piezoelectric coupling of quartz \([53]\). The calculation is performed by using numerical values for piezoelectric and stiffness coefficients at RT from Ref \([54]\), and for the same coefficients at 4K from Ref \([55]\). The corresponding ICTEs are calculated for the doubly-rotated quartz cut from values in Ref \([46]\), giving \(\alpha_1 \delta T = -2.54 \times 10^{-3}\), \(\alpha_2 \delta T = -2.124 \times 10^{-3}\) and \(\alpha_3 \delta T = -1.65 \times 10^{-3}\) for the temperature change from 300K to 4K. This calculation gives realistic fractional frequency changes from RT to 4K as the effective elastic constants \(\varepsilon_{4K}\) has to be adjusted by less than 2% to match the experimental results, that are \(+14.75 \times 10^{-3}\), \(+5.13 \times 10^{-3}\) and \(-1.37 \times 10^{-3}\) for A, B and C mode consequently (Appendix B). It may also be reminded that temperature coefficients of various parameters are lower than \(-10^{-8}\) for temperatures close to 4K.

The uncoated resonator can be seen as a circular plate subject to extra diametrically applied forces \(F\) coming from constrained contractions of its four bridges induced by cooling from RT to 4K. Assuming that the resonator rim is clamped, the naked device would exhibit a fractional frequency change \(\Delta f/k\) from the ideal reference state at 4K of \(-0.32 \times 10^{-3}\) for the A-mode, \(-0.18 \times 10^{-3}\) for the B-mode, and \(+1.86 \times 10^{-5}\) for the C-mode.

As mentioned above, the graphene layer is deposited on one side of the quartz substrate at room temperature, and then this initially stress-free hybrid device is cooled down at 4K. Estimated ICTE for graphene, \(+1.1 \times 10^{-3}\) from data by Ref \([56, 57]\), closer to \(+3.7 \times 10^{-3}\) from data by Ref \([49]\), should be compared with quartz crystal ICTE mentioned above. Consequently, the mismatch of CTE of these materials results in stresses and bending. This is true for a free expansion/contraction system and such induced stresses have to be added to stresses coming from the bridges. Comparing resulting frequency shifts for the case with and without graphene coating, the fractional frequency difference result in \(\frac{\Delta f_{4K}}{f_{4K}} \approx -1.7 \times 10^{-8}\), \(-1.1 \times 10^{-8}\), \(+1.3 \times 10^{-9}\) for the A, B, and C mode respectively (See Appendix B). These numerical values added to the mass-loading effect do not balance the constant value of the latter (calculated on the order of \(\frac{\Delta f_{300K} - \Delta f_{4K}}{f_{4K}} \approx -3 \times 10^{-7}\)) to explain the experimental values in Fig. 1. Finite-Element-Method (FEM) simulations have also been performed to estimate the stresses induced by the composite-device cooling using the set of CTE from Ref \([46]\) for the quartz substrate and Ref \([14]\) for the graphene layer. These simulations provide estimations of stresses similar to those obtained above by analytical modeling (a distribution of Von Mises stress is shown in Fig. 5).

In the same time analytical formulas can also be used to estimate stresses \(\sigma_1, \sigma_2, \sigma_3\), or at least their respective center values \(\sigma_i(0,0,0) = b_i\), from the knowledge of the
measured A, B and C-mode fractional frequency shifts. This is done by solving a set of three equations with three unknowns \( b_1, b_3, b_5 \):

\[
\frac{f_{4K,g1} - f_{4K,i}}{f_{4K,i}} = \frac{R_{3i}}{2} b_1 + \frac{R_{3i}}{2} b_3 + \frac{R_{3i}}{2} b_5 + \frac{\Delta f_{ML4K}}{f_{4K}},
\]

where \( i \) stands here for A, B and C modes, \( R_{ij} \) being force-frequency coefficients (See Appendix B), and the left hand side is given by experimental values from Fig. 2, and the theoretical mass-loading effect \( \frac{\Delta f_{ML4K}}{f_{4K}} \) is \(-3 \times 10^{-7}\). Solutions of this system are: \( \sigma_1(0) = +0.8\text{MPa}, \sigma_3(0) = -0.4\text{MPa}, \sigma_5(0) = +0.6\text{MPa} \).

It may be noticed that \( \sigma_3 \) differs significantly from \( \sigma_1 \) (\( \sigma_1 = \sigma_3 \) signifies isotropic case) and \( \sigma_5 \) is not negligible (zero expected in an isotropic case). These values could obviously be modified by taking a different value for the mass-loading effect, and it is not unreasonable to postulate that graphene contamination occurs by cryogenic trapping when cooling down the device. Thus, as an example, with \( \frac{\Delta f_{ML4K}}{f_{4K}} = -80 \times 10^{-7} \) (the assessed value extracted from measurement at RT) calculated stresses at the center would be \( \sigma_1(0) = -0.9\text{MPa}, \sigma_3(0) = -0.6\text{MPa} \) and \( \sigma_5(0) = +1.4\text{MPa} \). Also, \( \sigma_3(0) \) would be equal to \( \sigma_5(0) = -0.6\text{MPa} \) for \( \frac{\Delta f_{ML4K}}{f_{4K}} = -65 \times 10^{-7} \).

Such a discrepancy between expected and observed stresses might originate from some kind of buckling. Indeed, the central part of our device looks like an hyperstatic system with its four quartz bridges, and it can be postulated that a small dissymmetry in alignments or dimensions of the bridges reinforced by the fact that the graphene disk is not actually perfectly centred on the quartz surface. Moreover, beyond these possible causes of additional stresses, even a perfectly-machined substrate might be a subject to residual stresses coming from the graphene-monolayer deposition technique \[37\]. So, it seems impossible to properly unravel the origin of actual stresses among possible sources at this level of order of magnitude.

Stresses on the order of 0.5MPa inside the 1mm thick quartz substrate raises the question of the corresponding stresses in the 0.35nm thick graphene film. Indeed, the integral \( S \) of the stress through the thickness of quartz substrate, i. e. the force per unit width \[25\] is just \( b_i \) when stresses behave as \( \sigma_i(x_2) = a x_2 + b_i \), and should be such that \( |S| = \sigma \delta x_2 \), where \( \sigma \) is the average stress in the graphene film, in a free-expansion/compression composite graphene-on-quartz device. The resulting mean value \( |\sigma| = b_i \frac{\delta x_2}{2} \) is about 140GPa, that is to say slightly greater than values of intrinsic tensile strength reported for a suspended graphene membrane at RT, 130GPa \[59\, 60\]. Yield strengths at cryogenic temperatures are typically greater than that at RT for metals \[61\].

**IV. CONCLUSION**

The state-of-the-art quartz crystal resonator had the required sensitivity to operate as an ultra precise QCM. It was used to verify mechanical and thermal properties (data such as Young modulus, Poisson coefficient, CTE) of a graphene monolayer coating at liquid-helium temperature. Areal mass and a mismatch of CTE induces surface or volume stresses that in turn give an output frequency shift. Although the methodology has been proven by testing gold and chromium coatings, values involved in the case of a graphene monolayer are three orders of magnitude lower than those of a 50 nm thick chromium coating. Based on published constant values of graphene, the analysis of experiment results shows that effects of CTE mismatch are hidden by mass-loading effects which are themselves mixed with additional stress effects that could be attributed to structural dissymmetries and/or a basic impact of the graphene deposition process or both. Thus, unless certain published graphene constants might be questioned, it results that, first, the actual mass of the layer is likely greater than the expected one, possibly because of cryogenic trapping of particles, and second that additional mechanical stresses are generated in the quartz substrate and consequently in the graphene film or vice-versa. Their order of magnitude suggests that stresses in the graphene monolayer are about 140GPa, that is very close to an expected tensile strength. Also, mechanical loss of \( 80 \times 10^{-4} \) at 4K have been observed for a graphene monolayer coated on a substrate, and tested in the experimental conditions described above.

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Appendix A: MASS LOADING

To quantify the mass loading effect, let us consider an example of a infinite quartz plate of thickness \( t_q \) whose normal axis is \( y \) (subscript 2 in the following equations) with the origin \( (y = 0) \) in the centre of the thickness of the plate. The plate is infinitely coated on both sides with coating thickness \( t_i \) of a material of density \( \rho_i \). The boundary conditions at plate surfaces involve surface stresses \( \sigma_{2yi}(y = +t_i/2) = -\rho_i t_i \ddot{u}_i(t_i/2) \) and \( \sigma_{2yi}(y = -t_i/2) = +\rho_i t_i \ddot{u}_i(-t_i/2) \), where \( i = 1, 2, 3 \), for the C, A, and B modes respectively, \( \ddot{u}_i \) the second time-derivative of the displacement. In this case resonant frequency of thickness modes is given by:

\[
f_n = \frac{n}{2t_q} \sqrt{\frac{c_{2211}}{\rho_q}} \left[ 1 - \frac{4k^2_{2221}}{n^2\pi^2} - R \right] \tag{A.1}
\]

corresponding to a fractional frequency shift:

\[
\frac{f_n - f_{n0}}{f_{n0}} \approx \frac{\Delta f_n}{f_{n0}} \approx -(1 + \frac{4k^2_{2221}}{n^2\pi^2})R,  \tag{A.2}
\]

where \( f_{n0} \) denotes a frequency before coating, the odd integer \( n \) denotes the OT order, \( c_{2211} \) is an elastic coefficient modified by piezoelectricity (pointed out by the upper bar: \( c_{2n12} = c_{2n12} + c_{2e2}c_{2211} \) with \( c_{2e2}: \) piezoelectric coefficients, \( c_{2211}: \) electric permittivity), \( k_{2221} \) is the electromechanical coupling factor, and \( R \) is the ratio of the additive mass over the quartz mass i.e. \( R = \frac{2\rho_i t_i}{\rho_q t_q} \) in the case of a quartz substrate coated with layers on both faces.

Quartz is just lightly piezoelectric; so that for the SC cut at room temperature, the quantity \( k_{2221}^2 = \frac{\epsilon_{2211}^2}{\epsilon_{22}c_{2211}} \) can be estimated as \( 1.76 \times 10^{-3}, 2.18 \times 10^{-3}, 0.46 \times 10^{-3} \) for the A, B, and C modes respectively. Thus, the vibration is often seen from a pure mechanical point of view for which a simplified resonance frequency shift just reads:

\[
\frac{f_n - f_{n0}}{f_{n0}} = \frac{\Delta f_n}{f_{n0}} \approx -R,  \tag{A.3}
\]

and does not depend anymore on the vibrating mode type, A, B or C. This estimation approach has become popular in the QCM community, and known as Sauerbrey’s formula. A relative frequency shift between the uncoated and graphene-coated resonator at 4K, can be calculated as a function of \( R \) at 300K:

\[
\frac{\Delta f_{ML4K}}{f_{4K}} \approx \frac{-\rho_q t_q}{\rho_i t_i} - R_{300K}(1 + \alpha_j\delta T)(1 + \alpha_g\delta T) = \frac{-R_{300K}(1 + \alpha_j\delta T)(1 + \alpha_g\delta T)}{1 + 3\alpha_g\delta T(1 + \alpha_g\delta T)} \approx -R_{300K}(1 + (\alpha_1 - \alpha_g)\delta T + (\alpha_3 - \alpha_g)(\delta T)^2) \tag{A.4}
\]

where \( \alpha_j = \alpha_j(T) \) denotes coefficients of thermal expansion (CTE) at a temperature \( T \). Comparing results at 4K and 300K, infinitesimal component \( \alpha_j(T)\delta T \) should be replaced with the corresponding integrated version (ICTE) over the temperature range: \( \int_T^0 \alpha_j(T)dT, \quad T_0 = 300K \). Ref [40] provides relevant values for the integration of quartz expansion coefficients, giving \( \alpha_1\delta T - 2.54 \times 10^{-3} \), \( \alpha_3\delta T = -2.124 \times 10^{-3} \) for quartz crystal within the considered temperature range. Estimations of ICTE for the graphene layer varies depending on the reference source: it is \( \alpha_g\delta T = +1.1 \times 10^{-3} \) from data by Ref [56], whereas it is closer to \(+3.7 \times 10^{-3}\) from data by Ref [15]. It should be noted that graphene expands when cooled down while quartz contracts. As a result, the fractional frequency shift at 4K, Eq. (A.4), would be \(-R_{300K} \) multiplied by \(+0.9936\) or \(+0.9885\) depending on the reference source, that is \(-3 \times 10^{-4}\).

The above made calculations of the mass loading effect and especially the practice methodology could be validated by applying them to more traditional gold and chromium coatings. For this, we assume again that mass loading is the dominant effect, so the device acts somewhat like a QCM with metal layers rigidly coupled to the quartz resonator. For this purpose additional tests had been made with a 150nm-thick gold coating and a 50nm thick chromium coating over a similar area of 6 mm diameter at 4K. In both cases coatings were used as excitation electrodes. It should be noted though that films with such thicknesses exhibit properties, especially CTE, not so far from those of bulk materials [62]. Thus, since thin film properties at 4 K are not known, gold and chromium ICTE can be estimated from bulk material data [63] giving \(-3.3 \times 10^{-3}\) and \(-9.8 \times 10^{-4}\) respectively. The corresponding estimates of fractional frequency shifts \( \frac{\Delta f_{ML4K}}{f_{4K}} \) are about \(-2.2 \times 10^{-3}\) and \(-0.27 \times 10^{-3}\) respectively. As shown in Fig. 6 experimental frequency shifts can be fitted with linear functions of frequency \( f \) with a good agreement with calculated values.

Appendix B: EFFECT OF STATIC STRESSES

Effects of a static mechanical bias on elastic waves, i.e. small dynamic fields superimposed on a static bias, were intensively studied in 70’s-80’s [35] [31] after Thurston and Brugger works in 1964 [22]. In this work, we employ Sinha-Tiersten’s perturbation analysis limited to the perturbation of the elastic constants and not including dielectric or piezoelectric constant changes for example which can be justified by the weak piezoelectric coupling
TABLE I. Material parameters at 300K. For Quartz, $C_A$, $C_B$, and $C_C$ are the SC-cut effective stiffness coefficients of A, B and C modes respectively.

| Material       | Density $\rho$ (kg/m$^3$) | Quartz SC-cut $C_{ij}$ (GPa) @ RT | Young mod. $Y$ (GPa) | Poisson coeff. $\nu$ | Shear mod. $G = \frac{Y}{2(1+\nu)}$ (GPa) | Thickness $t$ (nm) |
|----------------|-----------------------------|------------------------------------|----------------------|----------------------|---------------------------------------------|------------------|
| Quartz [54]    | 2048                        | $C_{11} = 86.7 \; C_{13} = 16.8$ |                      |                      | $(C_A \approx 121)$                          | $1 \times 10^6$   |
|                |                             | $C_{13} = 109.9 \; C_{35} = 13.0$ |                      |                      | $(C_B \approx 41.5)$                          |                  |
|                |                             | $C_{51} = -13.64 \; C_{55} = 58.7$ |                      |                      | $(C_C \approx 34.5)$                          |                  |
| Au [65, 66]    | 19300                       |                                    | 75                   | 0.44                 | 26                                          | 150              |
| Cr [66]        | 7140                        |                                    | 275                  | 0.21                 | 115                                         | 50               |
| Graphene [24, 67] | 2200                      |                                    | 1000                 | 0.16                 | 430                                         | 0.35             |

FIG. 6. Frequency shift (difference between coated and uncoated cases) as a function of the frequency for various OTs of the three vibration modes for gold and chromium coatings on both sides of a plate measured at 4K. Solid and dashed lines correspond to the mass loading effect.

of quartz [53]. In accordance to this approach, the fractional frequency change, at frequency $f = \frac{\nu}{2\pi}$, induced by a bias can be expressed as, for a pure thermoelastic problem (for convenience, the abbreviated notation, or Voigt notation, is used as follows: a pair of indices like $ij$ is replaced with a single index according to $11 \rightarrow 1$, $22 \rightarrow 2$, $33 \rightarrow 3$, $23 \rightarrow 4$, $13 \rightarrow 5$, $21 \rightarrow 6$):

$$\Delta \omega = \frac{1}{2\omega} \int \frac{\delta \bar{E}}{\bar{E}} \int \frac{\delta \bar{u}_{\alpha}}{\bar{u}_{\alpha}} \ dV,$$

(B.1)

with

$$\delta \bar{E}_{kal\gamma} = c_{kaln} w_{\gamma,n} + c_{kml\gamma} w_{\alpha,m}$$

$$+ c_{kal\gamma a} w_{\alpha,b} + c_{klab} w_{\alpha,b} \delta_{\alpha \gamma},$$

(B.2)

where $c_{ijkl}$ and $c_{ijklmn}$ are the second and third order elastic stiffness coefficients respectively, $w_{ij}$ the bias displacement gradients, $u_i$ the vibration displacements, at room [68-70], within the volume $V$. The last term takes into account the fact that constants depend on temperature $T$, which is assumed to be homogeneous ($T_0$ being the reference temperature). The expression is limited to the first order derivatives of stiffness coefficients since temperature changes should also be small. It also has to be mentioned that In a real RAW cavity, the active part of the resonator is anchored to its supporting rim by means of four quartz bridges As a result in reality, the thermal contraction of the crystal resonator is not strictly free but rather constrained by these bridges.

Although Eq. (B.1) is usually applied at RT, it can also be utilised for the graphene induced stress at cryogenic temperatures. In this case, the resonator without graphene is used as a reference state assuming it is stress-free at 4K. So, an infinite flat plate vibrating at $f_n = \frac{\nu}{2\pi \sqrt{\rho}}$, and cooled down from RT to 4K would exhibit a fractional frequency change:

$$\frac{f_{4K} - f_{300K}}{f_{300K}} = \sqrt{1 + (\alpha_1 + \alpha_2 + \alpha_3) \delta T} \left(1 + \frac{\delta\bar{E}_{kal\gamma}}{\bar{E}} \delta T\right),$$

(B.3)

The calculation is performed by using numerical values for piezoelectric and stiffness coefficients at RT from Ref [51], and for the same coefficients at 4K from Ref [55]. The corresponding ICTEs are calculated for the doubly-rotated quartz cut from values in Ref [46], giving $\alpha_1 \delta T = -2.54 \times 10^{-3}$, $\alpha_2 \delta T = -2.124 \times 10^{-3}$ and $\alpha_3 \delta T = -1.65 \times 10^{-3}$ for the temperature change from 300K to 4K. This calculation gives realistic fractional frequency changes from RT to 4K as the effective elastic constants $c_{ijkl}$ have to be adjusted by less than 2% to match the experimental results, that are $+14.75 \times 10^{-3}$ for the A mode, $+5.13 \times 10^{-3}$ for the B-mode, $-1.37 \times 10^{-3}$ for the C-mode. It may also be reminded that temperature coefficients of various parameters are lower than $10^{-8}$ for temperatures close to 4K.

The perturbation tensor $\delta \bar{E}_{kal\gamma}$ can be expressed in terms of strains $E_{ij}$ by means of symmetry or antisymmetry properties of tensors as:

$$\delta \bar{E}_{kal\gamma} = c_{kaln} E_{\gamma,n} + c_{kml\gamma} E_{\alpha,m}$$

$$+ c_{kal\gamma a} E_{\alpha,b} + c_{klab} E_{\alpha,b} \delta_{\alpha \gamma},$$

(B.4)
Stresses and strains are related by the following linear (first order) thermoelastic constitutive equations as:

$$\sigma_i = c_{ij}[E_j - \alpha_j \delta T] = c_{ij}E^\alpha_j$$  \hspace{1cm} (B.5)

or in terms of strains. Introducing compliance coefficients $s_{ij}$, the following relation can be written:

$$E_j = s_{ij}\sigma_i + \alpha_j \delta T = E^\sigma_j + E^T_j,$$  \hspace{1cm} (B.6)

where $E^\sigma_j = s_{ij}\sigma_i$ being the stress-induced part of $E_j$ caused by external loads and displacements and/or non-uniformities in temperature or expansion properties, and $E^T_j = \alpha_j \delta T = \alpha_j(T(T - T_0))$ refers to strains caused by free thermal expansion for a given temperature change $\delta T$ replaced with its ICTE. The perturbation tensor can be calculated from a reference state at 4K by means of order elastic stiffness, unknown at 4K, from their values at RT \[54, 71\]. Thus, the perturbation tensor is limited to a thermostability part and can be written:

$${\hat{C}}_{i\hat{k}a\gamma} = c_{kaln}\gamma_{mn}\sigma_{me} + c_{mlb}\gamma_{abc}\sigma_{me} + c_{kalb}\gamma_{abc}\sigma_{me} + \delta_{ml}\delta_{abc}\sigma_{me} = \left[\begin{array}{c}
\left[c_{kaln}\gamma_{mn}\gamma_{me} + c_{kalb}\gamma_{abc}\gamma_{me} + c_{kalb}\gamma_{abc}\gamma_{ame} + c_{kalb}\gamma_{abc}\gamma_{ame}\right]
\end{array}\right].$$ \hspace{1cm} (B.7)

For the case of acoustic waves propagating along the thickness $y$-axis, or $x_2$, in a flat resonator (thus, with no variations along $x_1$ and $x_3$), the dynamic displacement gradients can be written:

$$u_{t,2} = \frac{\omega}{V_1} \cos \left[\frac{\omega}{v} x_2\right] \sin(\omega t),$$ \hspace{1cm} (B.8)

with $\frac{\omega}{v} = \frac{n\pi}{x_2}$, $n$ is the OT number, $v$ the propagation speed and $V_1$ the eigenvector of the mode of interest (normalised as $V_1V_1 = 1$). In addition, volume integrals in Eq. (B.1) can be reduced to integrals over the thickness at the center, where the wave amplitude is maximum due to trapping. Thus, the stress-dependent part of the frequency shift becomes:

$$\Delta \omega \approx \frac{1}{2\omega} \int_{t_{4}^{+}}^{t_{4}^{+}+\omega/2} K_{mc} \sigma_{mc}(0, x_2, 0) \cos^2 \left(\frac{\omega}{v} x_2\right) dx_2$$

$$\approx \frac{\omega}{2v^2} \int_{t_{4}^{+}}^{t_{4}^{+}+\omega/2} K_{mc} \sigma_{mc}(0, x_2, 0) \cos^2 \left(\frac{\omega}{v} x_2\right) dx_2$$

with

$$K_{mc} = 2c_{2n2}\gamma_{mn} \gamma_{me} V_1 V_2 + c_{2n2}\gamma_{abc} \gamma_{ame} V_2 V_3 + \delta_{2m}\delta_{2e}.$$ \hspace{1cm} (B.9)

This relationship is applied to coated and uncoated cases in the following discussions.

1. **Uncoated resonator**

The uncoated resonator can be seen as a circular plate subject to extra diametrically applied forces $F$ coming from constrained contractions of its four bridges induced by cooling from RT to 4K. A diametrical compression induces constant stresses $\sigma_i$ at the center of the quartz plate leading to a frequency shift:

$$\frac{\Delta \omega}{\omega} \approx \frac{1}{t_q \rho_q v^2} \int_{t_{4}^{+}}^{t_{4}^{+}+\omega/2} K_{s1} \sigma_1 \cos^2 \left(\frac{\omega}{v} x_2\right) dx_2$$

$$\approx \frac{1}{t_q \rho_q v^2} \frac{\sigma_1 t_{K_i}}{2} \approx \frac{\sigma_1}{2} R_i,$$ \hspace{1cm} (B.11)

where $i = 1, 3, 5, R_i = K_{i\alpha\gamma}$ are Ratajski coefficients \[72\]. The eigenvalue $\rho_q v^2$ and values of constants $K_i$ depend on the mode. Calculated values of these coefficients for the doubly-rotated SC-cut at 4K are given in Table II. Stresses at the center of a circular plate with radius $r_q$ can be adapted from Ref. \[73\] for a four-point mounting with bridge in the $x_1 - x_3$ plane to give:

$$\sigma_1 \approx \frac{2F}{\pi t_q r_q}$$ \hspace{1cm} (B.12)

while $\sigma_5 \approx 0$ for a SC-cut. The diametrically applied force $F$ can be calculated by stating that a diameter change $2\Delta r_q$ of the circular plate due to free thermal expansion/contraction from 300K to 4K is constrained by an equivalent change in bridge length $2\Delta l$ caused by some force $F$. In free thermal expansion/contraction the diameter change along $x_1$ is $2\Delta r_q = 2r_q\alpha_1 T$ at one end and clamped into place on the other end (this is an assumption at the rim), exhibits a length change $\Delta l = 0$ along the $x_1$ axis (the same approach is applied to the $x_3$ axis) gives:

$$F_1 = b t_q \sigma_1^2$$ \hspace{1cm} (B.13)

where $\alpha_1 \delta T$ denotes an ICTE. Consequently, assuming that the resonator rim is clamped, the naked device would exhibit a fractional frequency change $\Delta f_{MK}$ from the ideal reference state at 4K (see Eq. (B.11)) of $-0.32 \times 10^{-3}$ for the A-mode, $-0.18 \times 10^{-3}$ for the B-mode, and $+1.86 \times 10^{-5}$ for the C-mode.

2. **Coated resonator**

As mentioned above, the graphene layer is deposited on one side of the quartz substrate at room temperature, and then this initially (seemingly) stress-free hybrid device is cooled down at 4K. Consequently, the mismatch thermal expansion coefficients of these materials results in stresses and bending. This is true for a free expansion/contraction system and such induced stresses have to be added to stresses coming from the bridges. Free-expansion induced stresses at the center...
of the coated plate can be simplified as linear functions of the thickness coordinate \( x \). (See for example ref. [73], and this is also confirmed by FEM simulations), written

\[
\sigma_i(0, x, 0) = a_i x^2 + b_i.
\]

As a consequence, Eq. (B.9) becomes:

\[
\Delta \omega = \frac{1}{\omega q} \int_{-t_q/2}^{t_q/2} K_i \sigma_i(0, x, 0) \cos^2 \left( \frac{\omega}{4v} x^2 \right) dx = \frac{1}{t_q \rho q v^2} b_i t_q K_i \frac{x}{2} \approx \frac{b_i}{2} R_i,
\]

for \( i = 1, 3, 5 \).

Considering a simplified model of a quartz substrate as an isotropic material with a thin coating layer \( t_q \ll t_q \), both at homogeneous temperature \( T \) with no rigid rotation around the center of the plate [53], thermoelastic stresses due to mismatch of both ICTEs when cooling from \( T = T_0 = 300K \) down to \( T = 4K \) can be estimated as follows. Solving this bilayer plate as an axisymmetric problem, thermoelastic stresses gives \( \sigma_1 = \sigma_3 \) and \( \sigma_2 = \sigma_4 = \sigma_5 = \sigma_6 = 0 \). Without any external force in free expansion/contraction conditions, and assuming in-plane strains \( E \) are the same in the substrate and in the coating, the force (and moment) equilibrium are:

\[
\sigma_1 = \sigma_3 = \frac{N_q}{t_q} \left( 1 - \frac{6x^2}{v^2} \right),
\]

where the in-plane force \( N_{1q} = N_{3q} = N_q \) acting in quartz is related to that in the graphene coating \( N_q \) based on the relationship

\[
N_q + N_q = \frac{Y_q t_q}{1 - \nu_q} \left( E - \alpha_q \delta T \right) + \frac{Y_q t_q}{1 - \nu_q} \left( E - \alpha_q \delta T \right) = 0.
\]

From this equation involved forces can be simplified as:

\[
N_q = -N_q = \frac{Y_q t_q}{1 - \nu_q} \frac{t_q}{t_q} \left( \alpha_q - \alpha_q \delta T \right) = \frac{Y_q t_q}{1 - \nu_q} \left( \alpha_q - \alpha_q \delta T \right),
\]

because \( t_q \ll t_q \), even if the graphene Young modulus is much greater than that of quartz \( (Y_q \approx 1TPa) \). Following the approach discussed above, infinitesimal \( \alpha_q \delta T \) is replaced with corresponding ICTE \( \int_{T_q}^{T} \alpha_q \delta T \), or, equivalently, by \( \bar{\alpha}_q \Delta T \), where \( \bar{\alpha}_q \) is the average of respective CTEs over \( \{T_0, T\} \) [74].

The effect of the four-bridge clamping is taken into account like in the case of a uncoated quartz. It is argued that \( \Delta r_q + \Delta l = 0 \) along bridge axis very close to \( x_1 \) and \( x_3 \) and \( \Delta \nu_x/a_q = E \) for the strain \( E \) extracted from Eq. (B.15):

\[
E \approx \frac{Y_q t_q}{1 - \nu_q} \left( \alpha_q \delta T + \alpha_q \delta T \right).
\]

Here, the first term of the right-hand side of the equation can be identify as an excess strain \( \Delta E \) in comparison with the strain \( E \approx \alpha_q \delta T \) of a uncoated disk of quartz in free expansion/contraction. Consequently the corresponding applied diametrical force due to bridge clamping along \( x_1 \) (and similarly along \( x_3 \)) becomes:

\[
F_1 = \frac{Y_q t_q}{1 - \nu_q} \left( 1 - \nu_q \right) \frac{b_t r_q}{s_{11}} \frac{b_t r_q}{s_{11}} + \frac{b_t r_q}{s_{11}} \left( r_q + 1 \right) \alpha_1 \delta T.
\]

This force is very close to the calculated for an uncoated substrate because expansion/contraction stress effects due to the addition of the graphene layer are negligible due to \( Y_q t_q \ll Y_q t_q \).

Comparing resulting frequency shifts for the case with (Eq. (B.14)) and without (Eq. (B.11)) graphene coating, the fractional frequency difference is written as:

\[
\frac{f_{4K_G} - f_{4K}}{f_{4K}} \approx \frac{R_i}{2} \frac{Y_q t_q}{1 - \nu_q} \frac{t_q}{t_q} \left( \alpha_q - \alpha_q \delta T \right)
\]

and results in \( f_{4K_G} - f_{4K} \approx -1.7 \times 10^{-8}, -1.1 \times 10^{-8}, +1.3 \times 10^{-9} \) for the A, B, and C mode respectively, with values of ICTE already mentioned previously. These numerical values added to the mass-loading effect do not balance the constant value of the latter (calculated on the order of \( \Delta f_{4K} \approx -3 \times 10^{-7} \)) to explain the experimental values in Fig. 4.
S. Dhara, P. Pant, and M. M. Deshmukh, Nanotechnology 21, 165204 (2010).

[58] E. P. Eernisse, Journal of Applied Physics 43, 1330 (1972).

[59] G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A. C. Ferrari, A. K. Geim, K. S. Novoselov, and C. Galiotis, Small 21, 2397 (2009).

[60] C. Lee, X. Wei, J. W. Kysar, and J. Hone, Science 321, 385 (2008).

[61] Y. Tamarin, “Atlas of stress-strain curves,” (ASM international, 2002) p. 808 pages.

[62] A. E. Mag-isa, B. Jang, J.-H. Kim, H.-J. Lee, and C.-S. Oh, International Journal of Precision Engineering and Manufacturing 15, 105 (2014).

[63] G.K. White and J. G. Collins, Journal of Low temperature Physics 7, 43 (1972).

[64] R. J. Corruccini and J. J. Gniewek, “Thermal expansion of technical solids at low temperature. a compilation from literature,” (National Bureau of Standards Monograph 29, 1961) p. 22 pages.

[65] L. Wang and B. C. Prorok, NSTI Nanotech, 760 (2006).

[66] B. Merle, Ph. D. Thesis, Erlangen FAU University Press (2013).

[67] O. L. Blakslee and et al., nature nanotechnology 41, 3373 (2007).

[68] B. K. Sinha and H. F. Tiersten, Journal of Applied Physics 50, 2732 (1979).

[69] D. S. Stevens, H. F. Tiersten, and B. K. Sinha, Journal of Applied Physics 54, 1704 (1982).

[70] S. Ballandras, IEEE Trans. on Ultrasonics, Ferroelectrics, and Frequency Control 53, 2086 (2006).

[71] R. N. Thurston, H. J. McSkimin, and P. Andreatch, Journal of Applied Physics 37, 267 (1966).

[72] J. M. Ratajski, IBM Journal , 92 (1968).

[73] D. Janiaud, L. Nissim, and J.-J. Gagnepain, Proc. of the 32nd Annual Frequency Control Symposium , 169 (1978).

[74] J. W. Hutchinson, Harvard University, Cambridge, MA USA, Notes for a DCAMM course at Technical University of Denmark (1996).