Akademie věd
České republiky

Teze disertace
k získání vědeckého titulu ”doktor věd”
ve skupině věd chemických

Tuning the Properties of Two-Dimensional Materials

Komise pro obhajoby doktorských disertací v oboru **fyzikální chemie**

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Místo a datum: **Praha, 26. září 2025**

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Summary

The thesis summarizes my major contributions toward an advanced in-air characterization of two-dimensional (2D) materials via Raman and photoluminescence (PL) spectroscopies, various atomic force microscopy (AFM) techniques, and their combinations. The push for utilizing those methods beyond the simple fingerprinting of chemical composition and lattice structure (by Raman) or topography (by AFM) had been called for due to the few-nanometer thickness of 2D materials, which makes standard lab-based techniques like X-ray diffraction (XRD) almost unusable and necessitates to perform them in ultra-high vacuum (UHV) and/or with high-brilliance beams. In contrast, common Raman spectroscopy or AFM can be equally powerful, done in ambient conditions by easily trained users, non-destructively, and quickly. In addition, they enable a simple implementation of setups for *in-situ* measurements and are not commonly limited by the choice of substrate. It is, therefore, possible to easily explore one of the largest perks, and, at the same time, one of the biggest weaknesses of 2D materials—their extreme sensitivity to their environment and external perturbations. The ensuing tunability of the crystal and optoelectronic structures in their whole volume (being only a few atoms thin) even enlarges the potential of 2D materials with their already unique properties.

The structure of the thesis follows a logic similar to the preceding paragraph. First, after briefly introducing the materials and basic concepts at stake, Chapter 2 provides notable examples of what the aforementioned methods can provide and how they can be pushed beyond the trivial. Chapter 3 moves to influencing and controlling the 2D materials *via* the choice of their substrate material, separately for graphene and transition metal dichalcogenides (TMDCs). Finally, Chapter 4 offers the ultimate merging of the capabilities of Raman spectroscopy coupled with externally delivered mechanical deformation and electrochemical gating of the interrogated material.

It has to be noted that the selection of relevant works could have been expanded beyond those explicitly mentioned in the following text, discussing more minor—but not less important—details; however, such a broadened scope would dilute the main messages of the thesis: Raman spectroscopy is capable of accurately quantifying lattice deformation and Fermi level energy in graphene, even when they are entangled and the stress tensors are convoluted. However, it is essential to mind the lateral resolution of the measurement, where the measurements performed within the light diffraction limit can provide misleading information. To minimize the chances of data misinterpretation, the utilization of tip-enhanced spectroscopy (or another method reaching nanoscale resolution) is essential. Finally, the ability of methods like Raman

spectroscopy to provide relevant and accurate information is enabled only when preceded by *in-situ* measurements, where the external perturbation is delivered in a controlled and known manner.

1. Introduction

The first isolation of single-layer (1L) graphene through mechanical exfoliation from a graphite crystal by Novoselov *et al.* [1] opened a box of materials, whose unique properties do not cease to surprise scientists from across the fields of chemistry, physics, and beyond. The range of materials now prepared down to a 1L limit, even just by using the Scotch tape, spans metals (or semimetals like graphene), semiconductors (like TMDCs), and insulators (*e.g.*, hexagonal boron nitride, hBN) [2]. Graphene still remains the finest example of how remarkably the properties of the "parent" bulk layered material can change when its thickness is reduced to a single layer. Out of many, its Young's modulus of $\sim$1 TPa, the strength of $\sim$130 GPa [3], room-temperature charge-carrier mobilities as high as 350×10^3 cm^{2}V^{-1}s^{-1} [4], or thermal conductivity of $\sim5\times10^3$ Wm^{-1}K^{-1} [5] are exceptional and often the highest among known materials. These—and myriad other—traits make 2D materials very appealing for applications in many areas, from optoelectronics [6] to energy storage and conversion [7], even already finding their way to commercialization [8].

One of the most important features of 2D materials is their extraordinary responsiveness to external stimuli. These include the atmosphere around them [9], the substrate they rest upon [10, 11], and any perturbation like temperature [12], mechanical deformation [13, 14], or doping, both by extrinsic elements [15] and charge carrier doping [16]. The main reasons for such susceptibility are the "all-surface" nature of 2D materials, *i.e.*, their entire volume is directly in contact with the surrounding medium, and their low thickness, which makes their bending rigidity extremely small [17]. Such a high sensitivity of a material has its pros and cons. On the one hand, it enables controlling and tuning the properties of such material at will, for example, tailoring it for a particular application [14]. On the other hand, it severely complicates its reproducible preparation and subsequent device fabrication on a large scale [6].

Therefore, it is absolutely essential to be able to easily, quickly, and non-destructively monitor the state of the material, mainly in terms of lattice stress, structural defects, doping, and contamination from any preparation step. In this regard, many of the conventional inspection methods fail due to a variety of reasons: inadequate resolution, low detection sensitivity, the necessity of preparing the samples in a special, often not recoverable way, *etc*. However, over the past few years, it has become apparent that Raman spectroscopy can often provide the necessary information after proper analysis. In spite of the small thickness of the material (and thus the small sampling volume), resonance processes [18] and interference effects [19] enhance the Raman intensity of many 2D materials. In conjunction with PL

spectroscopy, which can be performed simultaneously with Raman spectroscopy, and with AFM-based methods, which have undergone significant instrumental progress over the past decade, the researchers obtained a powerful toolbox capable of providing access to many of the important properties listed above. And, if properly coupled onto the AFM tip, Raman and PL spectroscopies can provide information down to the nanometer limit, even in the ambient, through Tip-Enhanced Raman or PL Spectroscopies (TERS or TEPL) [20].

However, proper analytical practice and benchmarks must be established to fully exploit the capabilities of those methods. It is also of utmost importance to understand at which levels of measurement accuracy and lateral resolution the particular results can be interpreted. The *in-situ* experiments thus serve two purposes: (i) to gain more knowledge about the fundamental physico-chemical processes taking place in the material and at its interface to the surrounding, and (ii) to build proper analytical foundations for standardization of future characterization of the material's state.

2. Characterization

This chapter will highlight only a few notable examples of the otherwise very broad range of results, some of which are included in the following chapter because they focus more on addressing a particular phenomenon.

2.1. Raman Spectroscopy

→ N. S. Mueller*, S. Heeg, M. Pena-Alvarez, P. Kusch, S. Wasserroth, N. Clark, F. Schedin, J. Parthenios, K. Papagelis, C. Galiotis, M. Kalbac, A. Vijayaraghavan, U. Huebner, R. Gorbachev, O. Frank, and S. Reich*, "Evaluating Arbitrary Strain Configurations and Doping in Graphene with Raman Spectroscopy", ***2D Mater.*** 5, 015016 (2018).

As noted in the Introduction, Raman spectroscopy is nowadays one of the most utilized methods for the basic characterization of 2D materials. For graphene and several other most studied members of the 2D family (*e.g.*, MoS_2), Raman spectroscopy moved significantly towards advanced characterization, providing quantified information on the quality (number of defects), thickness (number of layers), charge doping (carrier concentration and/or Fermi energy), or strain (lattice deformation) [18]. However, while the evaluation of *e.g.*, defects or layer number, is rather straightforward, quantification of strain and charge doping is more complex. When focusing solely on graphene, the number of defects and their types are accessed through Raman modes, which are activated only by the presence of the defects themselves (D and D' modes). In contrast, both strain and doping are reflected in changes in peak

positions, widths, and intensities of the two Raman modes, which are always present in the graphene Raman spectra, namely the G and 2D modes. An approach using the correlation of G and 2D frequencies (ω_{G} and ω_{2D}) to separate the contributions of the two perturbations was proposed by Lee *et al.*[21]. However, this approach faces a serious drawback: the type of strain (biaxial or uniaxial) has to be known prior to the data analysis and can only be used to evaluate biaxial deformation. Otherwise, errors of up to one order of magnitude (of both strain level and carrier concentration) can arise due to the appearance of peak splitting (both for G and 2D) from uniaxial strain, where the intensities of the individual components are incident/scattered-light polarization dependent (for details, see section 4.1).

One way of circumventing this issue is to remove the data points clearly corresponding to the effects of uniaxial strain [22] and then evaluate the rest according to the original approach from ref. [21]. Unfortunately, this method does not enable the quantification of anisotropic strains and can still lead to inaccuracies. The crucial improvement, proposed and experimentally verified in the main publication related to this section (Mueller *et al.* [23]), involves the utilization of co-rotating circularly polarized light (both incident and scattered) to precisely determine the value of biaxial strain and charge doping from center-of-mass values of the G and 2D mode components in the ω_{G}–ω_{2D} plot. The circularly polarized light provides spectra with the full intensity of the individual components from anisotropic lattice deformation, regardless of the orientation of the strain. In contrast to the commonly used linearly polarized light, the correct center-of-mass value can be obtained. After the biaxial strain and charge doping are known, the frequency of the G mode at zero strain for the particular doping (ω_{G}^{0}) is obtained from the correlation plot, after which the shear component of the strain (ε_{s}) is calculated from the G peak splitting: $\Delta\omega_{\mathrm{G}}^{\mathrm{s}} = \omega_{\mathrm{G}}^{0}\beta_{\mathrm{G}}\varepsilon_{\mathrm{s}}$, where β_{G} is the shear deformation potential of the G mode [23].

As we have shown, the approach can be successfully utilized for quantifying doping and strain in unknown configurations in cases where the anisotropic stress component is small and only results in an apparent asymmetry of the Raman modes. In addition, the arbitrary strains can also be resolved in nanoscale resolution, if surface-enhanced Raman scattering is involved [23].

2.2. Atomic Force Microscopy

→ A. Rodríguez*, J. Varillas*, G. Haider, M. Kalbáč, and O. Frank*, "Complex Strain Scapes in Reconstructed Transition-Metal Dichalcogenide Moiré Superlattices", ***ACS Nano*** 17, 7787–7796 (2023).

→ Z. Hájková*, M. Ledinský, A. Vetushka, J. Stuchlík, M. Müller, A. Fejfar, M. Bouša,

M. Kalbáč, and O. Frank, "Photovoltaic Characterization of Graphene/Silicon Schottky Junctions from Local and Macroscopic Perspectives", ***Chem. Phys. Lett.*** 676, 82–88 (2017).

TMDCs can be exfoliated down to monolayer thickness, like graphene; however, in contrast to it, they are room-temperature semiconductors (in their most stable configurations) with strong photoluminescence in the visible and near-infrared. When stacking two TMDC monolayers into vertical heterostructures, charge transfer processes occur by forming a type-II band alignment. The twist angle, θ, between the two layers determines the optoelectronic properties of the resulting heterobilayer and the parameters of a superlattice that is formed on top of the individual crystal lattices of the individual layers. Such moiré superlattices then give rise to various interesting phenomena, including moiré excitons, ferroelectricity, the appearance of quantum wells, and others [24, 25]. Many of these phenomena are connected with the reconstruction of the individual layers' lattices, especially at small θ, which, in turn, translates to the emergence of considerable local deformation. While the moiré patterns can be visualized using high-resolution microscopy techniques, such as scanning transmission electron microscopy or scanning probe microscopy, there are large gaps in understanding the heterostrains appearing in the reconstructed lattices.

In our work, we focused on the θ-dependent stress fields in MoS_2/$MoSe_2$ heterobilayer [26]. We identified several spectroscopic fingerprints of the interaction between the two layers, namely the appearance of the otherwise Raman-inactive A_{2u} mode of $MoSe_2$ and the interlayer exciton in the PL spectra (these fingerprints are discussed in more depth in sections 3.2 and 2.3, respectively). The splitting of the Raman E^1_{2g} mode was pinpointed as the benchmark of the mixture of isotropic and anisotropic strains that materialize during lattice reconstruction at $\theta \sim 0$. The presence of both types of strain was evidenced by the polarization dependence of this mode, which showed partial oscillations in the intensities of the split-mode components. The spectroscopic study was corroborated by an extensive AFM characterization. The anisotropic variations of the moiré lattice at small θ angles were visualized through fast-Fourier-transform analysis of the topography and stiffness channels. Domains with AA and AB/BA stacking were identified in the AFM images for moiré periodicities even below 10 nm. Large-scale molecular dynamics simulations confirmed the atomic-level lattice reconstruction for small θ angles as well as the presence of local strains, which decreased with increasing θ [26].

The versatility of AFM was showcased in a study where conductive AFM (C-AFM) was utilized to assess photovoltaic characteristics of a graphene/silicon Schot-

tky junction [27]. The Schottky junction solar cells were prepared by transferring graphene grown by chemical vapor deposition (CVD) onto hydrogenated amorphous and microcrystalline silicon with etched oxide layers. Characterization by C-AFM under illumination was compared against standard measurements using a solar simulator. Local photocurrent (I) maps at discrete bias (V) steps were obtained, from which the average I values were extracted to reconstruct pseudo I-V curves. From the curves, fill factor and open-circuit voltage (V_{OC}) were evaluated and compared against values obtained by the solar simulator at AM1.5G. The fill factor values were comparable from the two methods, with less than 10% variation. The V_{OC} values were consistently lower from the C-AFM; however, the relative scaling, *e.g.*, between measurements performed on aged samples, was maintained the same as from the solar simulator. It should be noted that the short-circuit current was not quantified due to the impossibility of precisely determining the illumination area in C-AFM measurement. The very good correlation between both independent techniques unequivocally proved C-AFM as a highly useful tool for photovoltaic characterization on nano- and micrometer scales [27].

2.3. Tip-Enhanced Spectroscopy

→ A. Rodríguez, M. Kalbáč, and O. Frank*, "Strong Localization Effects in the Photoluminescence of Transition Metal Dichalcogenide Heterobilayers", ***2D Mater.*** 8, 025028 (2021).

→ A. Rodríguez, A. Krayev, M. Velický, O. Frank*, and P. Z. El-Khoury*, "Nano-Optical Visualization of Interlayer Interactions in WSe_2/WS_2 Heterostructures", ***J. Phys. Chem. Lett.*** 13, 5854–5859 (2022).

As mentioned in the previous section, TMDC heterobilayers have garnered considerable attention over the past few years due to the numerous interesting phenomena they exhibit. The interlayer excitons (IEX) belong to one of them. They form when two TMDC layers have a strong interaction, resulting in a type-II band alignment, where electrons and holes from one intralayer exciton can migrate to the lower-lying conduction band and higher-lying valence band of the second layer, respectively. Consequently, the thus-formed recombined exciton will have a lower energy than the two intralayer ones and can thereby be distinguished in the photoluminescence spectra of the heterobilayer. The presence of IEXs has been commonly documented by standard micro-PL measurements, *i.e.*, with lateral resolution above the light-diffraction limit. Such measurements, however, do not provide enough information on where the IEXs reside spatially, which can be crucial due to the known heterogeneity of the interface caused by contamination trapped during the stacking procedure [28]. Tip-enhanced

spectroscopies [29] or scanning near-field microscopies [30] belong to the few capable of providing the needed localized information.

We studied the local PL signatures in various heterobilayers composed of MoS_2, WS_2, $MoSe_2$, and WSe_2 using tip-enhanced photoluminescence, with a lateral resolution down to 30 nm [31]. Most of the TMDC layer combinations showed the expected IEX signals in the perfectly flat parts of the samples. In contrast, no IEXs were observed from various topographic features like bubbles or blisters. Here, only the intrinsic excitons from the individual layers were present but often shifted, or at least asymmetrically broadened, towards lower energies. Such shifts evidence tensile deformation of the lattice in the top layer, which is strained by the contamination trapped in between. This was verified by reversing the stacking order of the two layers, where again, only the intralayer excitons from the top layer experienced redshift.

The most important finding related to the MoS_2-WSe_2 heterobilayer. In this system, the IEX was repeatedly reported at an energy (1.55 eV) very close to the intrinsic WSe_2 exciton (1.65 eV) [32, 33]. However, as found in our study, these signals originate, in fact, also just from bubbles and blisters in the top WSe_2 layer, and they are completely absent when MoS_2 is on top. We proved that due to PL enhancement, when the layers are decoupled, even a single nanobubble with 60 nm diameter in an otherwise perfectly flat area of 1×1 µm^2 can induce a PL emission very similar to those reported in the mentioned papers as IEX. In such cases, the flat area is void of any features at the given energy. Instead, here, the IEX appears at a much lower energy of ~ 1 eV [31]. These observations emphasize the need for highly resolved spectroscopic measurements and a careful interpretation of experiments conducted by microscale methods on samples with nanoscale heterogeneities.

The interactions within a TMDC heterobilayer were the subject of another study, this time with plasmonic materials on both the substrate and the AFM tip (gold and silver), thereby localizing the near-field even more than by just using a plasmonically active tip as in the previous work. The so-called "gapped mode" enabled measurements of enhanced Raman spectra localized down to 5 nm lateral resolution [34]. As a downside, the PL was almost completely quenched due to charge transfer to the metallic substrate. Nevertheless, similar to the TEPL study, major differences were discerned between flat and perturbed areas, like nanobubbles. In the flat areas, the strong interaction between the layers was evidenced by the presence of the interlayer phonons in the ultra-low frequency spectra range at ≈ 22 cm^{-1} Raman shift and the symmetry-activated A_1 mode of 1L WS_2 (A_{2u} in the notation of bulk WS_2). The Raman mode symmetries and how they reflect the interaction are discussed in more

detail in section 3.2. In contrast, the spectra from nanobubbles showed neither of these features but increased intensity of the normal Raman modes of WS_2. In addition, 2D cross-correlation analysis showed a positive correlation of this mode's intensity with a weak red-shifted PL signal of WSe_2, corresponding to the tensile strain in the bubble [34].

3. Interaction with Substrates

A substrate, or the lack of it, is one of the main factors determining the properties of the 2D material resting on it. The substrate can either be "native", *i.e.*, the sample was prepared (grown, exfoliated) on it, or "secondary", *i.e.*, the sample was transferred to it. The material, its lattice, the surface geometry, or contamination on it all influence the 2D material and the level of interaction between them. In the following sections, two important cases for graphene (one for grown and one for exfoliated samples) will be described, followed by a very recent set of studies focusing on the interaction between TMDCs and bulk metals.

3.1. Graphene

→ O. Frank*, J. Vejpravová, V. Holý, L. Kavan, and M. Kalbáč, "Interaction between Graphene and Copper Substrate: The Role of Lattice Orientation", ***Carbon*** 68, 440–451 (2014).

→ K. Sampathkumar, C. Androulidakis, E. N. Koukaras, J. Řáhová, K. Drogowska, M. Kalbáč, A. Vetushka, A. Fejfar, C. Galiotis*, and O. Frank*, "Sculpturing Graphene Wrinkle Patterns into Compliant Substrates", ***Carbon*** 146, 772–778 (2019).

Chemical vapor deposition (CVD) remains the method of choice for producing large-area monolayer graphene with a quality that approaches that of mechanically exfoliated flakes. However, the commonly used growth substrate, namely polycrystalline copper foils, leads to CVD graphene with many grains and, thus, grain boundaries, which negatively influence the mechanical and electronic properties of the samples. One way, albeit a more costly one, to avoid the grain boundaries is to use Cu single crystals for the growth. At the same time, it is important to understand how the different Cu lattice orientations influence graphene's crystal structure and its other properties, even when the polycrystalline foil is utilized for the growth.

To perform the study, graphene was grown by CVD on Cu single crystals with (100), (110), and (111) faces and on common Cu foils [35]. Without transferring, the as-grown graphene was investigated by extensive micro-Raman mapping, combined with X-ray diffraction techniques and AFM, to assess the underlying crystal qual-

ity and surface topography, respectively. The simplified ω_G–ω_{2D} analysis [21] was utilized to examine the spread of the Raman frequencies (and, thus, the spatial homogeneity of the sample at scales larger than the laser spot) and the strain and doping levels. The width of the peaks reflected the spatial homogeneity at scales below the spot size. The results clearly showed that the grown graphene is highly and distinctly susceptible to the substrate's lattice orientation. As expected, the single-crystalline substrate provided more homogeneous graphene, regardless of the particular lattice orientation. Cu(111) produced a flat and uniformly compressed graphene ($\sim$0.3% of biaxial deformation) with electron doping ($\sim$250 meV Fermi level shift). Graphene on Cu(110) was heterogeneously compressed (0.05–0.3%) with minimum charge doping. Graphene on Cu(100) was uniformly slightly compressed ($\sim$0.1%) and with highly defined regions with distinctive doping levels ($\sim$0, 250, and 350 meV). These observations corresponded to the previous reports, which utilized other, mostly UHV-based methods, and highlighted the applicability of Raman spectroscopy for quantitative analysis of graphene [35]. The obtained knowledge was later expanded and utilized in *e.g.*, studying lattice orientation-dependent functionalization of graphene [36].

Understanding the interaction of graphene with polymers is essential for leveraging the extreme mechanical properties of graphene in functional composites. The role of polymeric supports in studying the fundamental properties of graphene will be examined in section 4.1; however, graphene can also actively participate in shaping the underlying matrix. The fabrication process for sculpturing wrinkled structures into soft polymers by thermal treatment of graphene and the ensuing mutual interaction between the components was described in ref. [37]. Both mechanically exfoliated and transferred CVD-grown graphene were shown to induce wrinkles in different soft polymers, with dimensions and orientation depending on the graphene thickness and aspect ratio of the flakes. The system can be described by models based on common stiff thin films on compliant substrates. The wrinkle wavelength, λ, is linearly related to the thickness of graphene, t: $\lambda = 2\pi t(E/3E_S^*)^{1/3}$, where E is the Young's modulus of graphene and E_S^* is the modified modulus of the polymer. The relation between λ and the amplitude of the wrinkles, A, is then also linear and determined by the amount of strain, ε, imposed on the system: $\varepsilon = (A\pi/2\lambda)^2$. The orientation of the wrinkles was controlled by the graphene geometry: long and narrow flakes exhibit perfectly parallel wrinkles, while low aspect-ratio flakes resulted in random patterns. The wrinkles imprinted into the polymer were retained even after the graphene removal. The fabrication process can thus serve as a simple way to pattern the surface of soft polymers with wavelengths as low as 50 nm. From the

fundamental perspective, we showed that the wrinkling does not heterogeneously influence the level of charge doping between the polymer and graphene; the surface potential measured by Kelvin-probe force microscopy (KPFM) did not show any fluctuations across the wrinkles and only reflected the thickness of graphene. The investigation of the wrinkles close to the flake's edges also revealed the presence of wrinklons, *i.e.*, the hierarchical transition zones where two smaller wrinkles merge into one larger. An analytical model describing the evolution of the wrinklons, based on energy principles, was later developed [38]. From the applied viewpoint, the compliant wrinkles serve as interlocks, which enhance the ability of graphene to withstand loading in composites through an efficient stress transfer between the graphene and its polymeric matrix [39].

3.2. Transition Metal Dichalcogenides

→ M. Velický*, A. Rodriguez, M. Bouša, A. V. Krayev, M. Vondráček, J. Honolka, M. Ahmadi, G. E. Donnelly, F. Huang, H. D. Abrunña, K. S. Novoselov, and O. Frank*, "Strain and Charge Doping Fingerprints of the Strong Interaction between Monolayer MoS_2 and Gold", ***J. Phys. Chem. Lett.*** 11, 6112–6118 (2020).

→ M. Velický*, G. E. Donnelly, W. R. Hendren, W. J. I. DeBenedetti, M. A. Hines, K. S. Novoselov, H. D. Abruña, F. Huang*, and O. Frank*, "The Intricate Love Affairs between MoS_2 and Metallic Substrates", ***Adv. Mater. Interfaces*** 7, 2001324 (2020).

→ A. Rodriguez*, M. Velický, J. Řáhová, V. Zólyomi, J. Koltai, M. Kalbáč, and O. Frank*, "Activation of Raman Modes in Monolayer Transition Metal Dichalcogenides through Strong Interaction with Gold", ***Phys. Rev. B 105***, 195413 (2022).

→ L. Pirker*, J. Honolka*, M. Velický*, and O. Frank*, "When 2D Materials Meet Metals", ***2D Mater.*** 11, 022003 (2024).

The isolation of individual atomically thin monolayers, *i.e.* 2D materials, from their parent bulk layered crystals opened up whole new fields in nanoscience and nanotechnology. On the one hand, the original, commonly used Scotch-tape method to prepare samples on dielectric substrates like SiO_2 results in small layers, rarely exceeding the first tens of micrometers in lateral dimensions. On the other hand, growth methods (like CVD) often yield large layers, but with abundant defects. Recently, a metal-mediated exfoliation technique opened a new route to obtain monolayers, whose lateral dimensions are essentially limited only by the size of the parent crystal (commonly centimeters) [40]. However, the peculiar, strong interaction between the 2D material and the underlying metal has remained underexplored, with almost no knowledge existing in 2020, in the early years after the method discovery. Systematic analysis of a large sample set of MoS_2 exfoliated on gold with varying thickness and

roughness and utilization of spectroscopy techniques with resolution ranging from micro- to nanoscale allowed us to postulate the first comprehensive hypothesis on how the MoS_2 locally interacts with its uneven Au substrate [41]. We identified the specific vibrational and binding energy fingerprints of this interaction using Raman and X-ray photoelectron spectroscopy, which indicated substantial strain and charge doping in the exfoliated MoS_2. TERS revealed heterogeneity of the MoS_2-Au interaction at the nanoscale, reflecting the spatial nonconformity between the two materials.

The study was later expanded to include also other metals, besides Au, as substrates for the exfoliation [42]. Surprisingly, even though the predicted binding energies between MoS_2 and most common and precious metals should lead to stronger interactions than in the MoS_2-Au system [43], Au still outperformed all the other metals in terms of monolayer exfoliation yields, when done in air. We explained the results by the ability of Au to resist oxidation, which, even for other precious metals, quickly quenches the interaction with MoS_2. Based on the downshift of the Raman E mode, we also postulated a hypothesis that interfacial strain in the metal-MoS_2 heterostructures is one of the critical factors facilitating the exfoliation, which has recently been confirmed [44].

Similar to the case of mutual interaction in TMDC heterobilayers (section 2.2), the interaction of TMDCs with metals is also reflected in the appearance of specific Raman spectroscopy fingerprints. They include the strain-induced downshift of the E mode, and interaction heterogeneity-driven apparent splitting of the A_1 mode, where the lower-frequency component is downshifted due to charge doping and bond weakening [41]. In addition, lowering the symmetry from D_{3h} (in freestanding TMDC monolayers) to C_{3v} (in monolayers interacting with the metals) results in the activation of the otherwise geometry-forbidden E (with E'' symmetry in free 1L) and symmetry-forbidden A_1 mode (with A_2'' symmetry in free 1L) [45]. The universal nature of these spectral fingerprints was confirmed for all members of the (Mo,W)(S,Se)$_2$ TMDC family by standard micro-Raman spectroscopy as well as TERS with variable contact setpoint.

Further aspects of the 2D materials-metals interactions, including controversies, open questions, and prospects of interaction-driven phase transitions and their implications for smart contact design, were discussed in a recent invited review [46].

4. External Perturbation

This chapter describes three sets of *in-situ* experiments, through which various aspects of properties of graphene and TMDCs were studied by Raman and/or PL

spectroscopy. The first two sections are focused on mechanical deformation, imposed uniaxially, either in-plane or out-of-plane. The last section explores charge doping in an electrolyte solution, performed locally, through a microdroplet spectroelectrochemical setup.

4.1. In-Plane Deformation

→ O. Frank, G. Tsoukleri, J. Parthenios, K. Papagelis, I. Riaz, R. Jalil, K. S. Novoselov, and C. Galiotis*, "Compression Behavior of Single-Layer Graphenes", ***ACS Nano*** 4, 3131–3138 (2010).

→ O. Frank, M. Mohr, J. Maultzsch, C. Thomsen, I. Riaz, R. Jalil, K. S. Novoselov, G. Tsoukleri, J. Parthenios, K. Papagelis*, L. Kavan, and C. Galiotis, "Raman 2D-Band Splitting in Graphene: Theory and Experiment", ***ACS Nano*** 5, 2231–2239 (2011).

→ O. Frank, G. Tsoukleri, I. Riaz, K. Papagelis, J. Parthenios, A. C. Ferrari, A. K. Geim, K. S. Novoselov, and C. Galiotis*, "Development of a Universal Stress Sensor for Graphene and Carbon Fibres", ***Nat. Commun.*** 2, 255 (2011).

→ O. Frank*, M. Bouša, I. Riaz, R. Jalil, K. S. Novoselov, G. Tsoukleri, J. Parthenios, L. Kavan, K. Papagelis*, and C. Galiotis, "Phonon and Structural Changes in Deformed Bernal Stacked Bilayer Graphene", ***Nano Lett.*** 12, 687–693 (2012).

→ J. Varillas*, J. Lukeš*, A. Manikas, J. Maňák, J. Dluhoš, Z. Melníková, M. Kalbáč, C. Galiotis*, and O. Frank*, "Mechanical Response of Monolayer Graphene Via a Multi-Probe Approach", ***Int. J. Mech. Sci.*** 273, 109208 (2024).

Soon after fundamental mechanical properties of graphene had been established [3], the intent of utilizing its exceptionally high Young's modulus and yield strength in composites necessitated the development of methods capable of assessing the changes in graphene's lattice and the stress transfer to/from the composite's matrix. Raman spectroscopy was selected as the first choice thanks to its capability of quickly and non-destructively monitoring the state of graphene even inside the composites. The first experiments utilizing *in-situ* Raman spectroscopy were done only during tensile deformation, either by direct stretching on a polyethylene terephthalate (PET) substrate [47] or by four-point bending on an acrylic beam covered by a photoresist (SU-8) [48], with the Raman shift rate per unit of nominal strain imposed on the substrate differing by a factor larger than two. The variation in the reports led to discord and increased efforts to properly determine the shift rates, which reflect the Grüneisen parameters (γ) and deformation potentials (β) of the Raman modes. The choice of substrate later proved to be crucial. On PET, the adhesion of graphene is low due to the surface structure of the plastic, while on SU-8 and similar three-dimensionally crosslinked polymers, the adhesion and ensuing interfacial shear strength (ISS) are

significantly higher.

To verify the hypothesis and to obtain the correct γ and β values, we set up an experiment using a cantilever-beam bending apparatus, which, in contrast to the setups above, allows for both tensile and compressive loading in one full cycle while still monitoring the same spot on the sample [17]. We also tested several types of substrate polymers, both with and without a top protective layer, which turned out to be essential for maintaining the ISS level longer. We confirmed the Raman shift rates for the G and 2D modes of graphene (and thus γ and β values) that had been reported in ref. [48] for tension and also for the initial stages of compression, including the splitting of the G mode due to symmetry lowering of the doubly degenerate E_{g} phonon [17]. For the first time, we reported the buckling failure in compression and linked the critical strain to the graphene flakes' geometries and the substrate. For flakes fully embedded between the polymer layers, the bending rigidity was found to be six orders of magnitude higher than for flakes suspended in air [17]. The link between critical strain values and the flakes' dimensions was afterwards corrected to account only for their length along the strain axis, showing that for flakes longer than ~ 4 μm, the critical strain remains $\sim 0.6\%$, and it only decreases for shorter flakes [49].

We further extended the investigations of graphene under uniaxial tensile loading by employing the 785-nm Raman excitation wavelength that not only confirmed the previously reported behavior but also revealed a pronounced splitting of the 2D Raman band, already at lower strain levels of $\sim 0.2\%$ [50]. In contrast to the simple origin of the G mode splitting, the splitting of the 2D mode has more complex roots stemming from inequivalent inner and outer scattering processes along paths between different K and K' points in graphene's Brillouin zone. The inequivalency increases with rising uniaxial lattice deformation, and the various branches provide different Raman intensities under specific incident/scattered light polarization [50]. Notably, the intensities of the individual processes also depend on the excitation wavelength, and thus on the shape of both the electron and phonon dispersions, which are progressively more trigonally warped from a perfect circle as the energy from the Dirac point increases. This results in a wavelength-dependent level of the 2D mode splitting, which becomes barely discernible with lower excitation wavelengths like 514 or 532 nm [50, 51].

A direct practical utilization of knowing the Raman response of graphene to uniaxial strain can be found in assessing the stress imposed onto carbon fibres, which are the core of modern structural lightweight composites. Through *in-situ* monitoring

of the Raman G band of carbon fibres with various morphologies under uniaxial stretching, we found that a universal value of average phonon shift rate with stress of $-5\omega_0^{-1}$ ($\mathrm{cm^{-1}MPa^{-1}}$), where ω_0 is the G band frequency at zero stress, can be derived both for graphene and carbon fibres, at least those with annular morphology (where the graphene stacks are arranged concentrically around the fibre axis) [52]. For fibres with radial morphology (where the graphene planes are stacked radially from the centre towards the fibres' rim), the phonon stress sensitivity is influenced by a dominance of the split G mode towards the component with a lower shift rate. Overall, a similar stress sensitivity, albeit influenced also by chirality, can also be found in carbon nanotubes [52].

The mechanical properties and behavior under loading of monolayer graphene can also be extended to graphene bilayers [53]. The split G band components shift at exactly the same rate in 2L as in 1L graphene, and the overall shift of the 2D band is also comparable. However, the 2D band in 2L graphene is already composed of 4 components corresponding to the phonon scattering processes involving electrons between the split conduction and valence bands. Therefore, it was not possible to directly discern the 2D mode splitting as in the case of the 1L graphene with the near-infrared excitation wavelength, but only indirectly via monitoring the relative intensities of the individual intrinsic 2D components [53]. An exception from the otherwise similar behavior of 2L could have been found locally, at spots where the two layers slightly decoupled at the step edge due to the imposed stress. In such regions, breaking of the inversion symmetry between the layers resulted in an additional splitting of the G mode due to the activation of otherwise only infrared-active E_u mode [53]. It would be tempting to assume that the symmetry breaking might also lead to a band gap opening, likewise to asymmetrically gated 2L graphene [54]; however, it was not possible to provide direct experimental evidence for such an effect.

All the above-mentioned works rely solely on Raman spectroscopy. While it is perfectly capable of determining the level of lattice deformation, it does not allow for assessing the force imposed on the tested specimens, for example, to quantify Young's modulus, strength, *etc.* Conversely, experiments that rely only on direct measurements of force-distance (F-d) curves often suffer from inaccuracies caused by imperfect clamping of graphene, which hinders correct evaluation of the deformation. Measurements performed with an AFM tip indenting suspended layers on circular holes mostly circumvent the adhesion problem [3], but the data analysis necessitates simplifications in terms of indenter size and shape, and complex stress distribution,

which can also lead to inaccuracies [55]. One potential solution is to employ a direct pulling mechanical system (to measure the F-d curves) with an independent gauge to quantify the deformation. To this end, we combined push-to-pull testing using a nanomechanical device and an indentation system capable of reaching sensitivity down to nN and nm ranges, *in-situ* with scanning electron microscopy (SEM) and Raman spectroscopy (also inside the SEM chamber) [56]. We demonstrated that using only the F-d approach, the Young's modulus values are underestimated by up to approximately one order of magnitude. When using the F-d approach to determine the deformation, but in conjunction with SEM or Raman to measure the actual effective width of the stretched graphene stripe, the Young's modulus values are still underestimated by a factor of four. Only the combination of using F-d curves to quantify the force, SEM or Raman to evaluate the effective width, and Raman to determine the actual deformation led to Young's modulus values on par with theory (1.04 ± 0.29 TPa) [56]. The difference can be explained by a joint effect of imperfect adhesion on the end clamps, causing slippage, and progressive reduction of the effective width due to cracking from the edges. Our molecular dynamics simulation also showed that the cracks tend to nucleate more on high-energy grain boundaries rather than on single point defects (carbon atom vacancies) [56].

4.2. Out-of-Plane Deformation

→ M. Peña-Álvarez, E. del Corro*, A. Morales-Garcia, L. Kavan, M. Kalbáč, and O. Frank*, "Single Layer Molybdenum Disulfide under Direct out-of-Plane Compression: Low-Stress Band-Gap Engineering", ***Nano Lett.*** 15, 3139–3146 (2015).

→ E. del Corro*, M. Peña-Álvarez, K. Sato, A. Morales-Garcia, M. Bouša, M. Mračko, R. Kolman, B. Pacáková, L. Kavan, M. Kalbáč, and O. Frank*, "Fine Tuning of Optical Transition Energy of Twisted Bilayer Graphene Via Interlayer Distance Modulation", ***Phys. Rev. B*** 95, 085138 (2017).

Out-of-plane deformation of micro-sized (or smaller) samples is commonly conducted in a hydrostatic setup, using an anvil cell with a smaller pressure chamber formed by a thin perforated gasket placed between the two anvil cullets and filled with a pressure-transmitting medium (PTM). In the case of monolayer materials like graphene, such an arrangement is challenging for the investigation of suspended samples, and a substrate is needed to support the specimen, potentially representing an additional cause of misinterpretation [57]. When the anvil cell (with the sample on a support) is utilized directly, *i.e.*, without PTM, the pressure acts only uniaxially, normal to the plane, while the sample is allowed to expand through the Poisson effect.

The differences these two methods (hydrostatic and uniaxial) have on a sample

can be quite profound. We showed, using the uniaxial setup with *in-situ* Raman and PL measurements, that 1L MoS_2 undergoes the transition from a semiconductor state with a direct band gap to an indirect band gap already at a very low pressure of < 1 GPa [58], in contrast to hydrostatic compression, where the same transition takes place at ≈ 22 GPa [59]. According to hints in the spectroscopy data and to density functional theory (DFT) calculations [58], the transition from semiconducting to semimetallic state occurs at ~ 3 GPa in the uniaxial case, while the same was predicted at > 60 GPa for the hydrostatic compression [59]. Further DFT calculations showed similar pressures needed for the transitions, also for the other members of the $(Mo,W)(S,Se)_2$ family [60].

Modulation of the optoelectronic structure of twisted bilayer graphene (tBLG) was shown through tracking the local maxima in the electronic density of states (DOS) during uniaxial out-of-plane compression. The relative twist angle between the two layers of tBLG causes zone folding, which results in the appearance of local Van Hove singularities (VHs) in the DOS. The energy levels of VHs are twist angle dependent, and they cause a manifold intensity increase of the Raman G band of tBLG when excited at the corresponding energy [61]. We monitored the evolution of the G band intensity of graphene tBLG samples with different twist angles, ranging from ≈ 10 to 13°, with excitation wavelengths from 488 to 647 nm, under uniaxial out-of-plane compression up to 2 GPa [62]. We found that the maxima in G band intensity for the different twist angles were both pressure- and excitation-dependent. With the help of DFT, it was found that the energy of VHs for tBLG with a particular twist angle depends non-monotonically on the distance between the layers. Due to the method of sample preparation, where the two graphene layers are stacked one upon the other sequentially, using a sacrificial polymer layer, the interlayer distance is always larger than the predicted equilibrium separation, reaching up to 1 nm. The compressive force then brings the two layers closer, thereby modulating the VHs energy and the associated optical transition by as much as 200 meV [62].

4.3. Electrochemical Gating

→ M. Jindra, M. Velický*, M. Bouša, G. Abbas, M. Kalbáč, and O. Frank*, "Localized Spectroelectrochemical Identification of Basal Plane and Defect-Related Charge-Transfer Processes in Graphene", ***J. Phys. Chem. Lett.*** 13, 642–648 (2022).

→ G. Abbas, F. J. Sonia, M. Jindra, J. Červenka, M. Kalbáč, O. Frank*, and M. Velický*, "Electrostatic Gating of Monolayer Graphene by Concentrated Aqueous Electrolytes", ***J. Phys. Chem. Lett.*** 14, 4281–4288 (2023).

In-situ Raman spectroelectrochemistry has a firm stand among highly efficient

methods to explore structural and chemical changes in electrochemically active materials. However, up till now, most of the experimental progress has followed the advances in Raman spectroscopy instrumentation. Whereas microspectroscopy enabled studies with lateral resolution down to the diffraction limit, the electrochemical resolution lagged behind. This divergence became highly acute when 2D materials, whose edges and basal planes have completely different electrochemical behavior, came into focus. The majority of *in-situ* Raman spectroelectrochemical investigations of graphene have been conducted on CVD-grown graphene with abundant grain boundaries or on exfoliated graphene, but in a macroelectrochemical cell with the edges of the flakes at least partially exposed to the electrolyte solution [16]. To address the lateral resolution discrepancy, we introduced a novel spectroelectrochemical method, where not only the Raman but also the electrochemical side is localized down to the micrometer scale. We showcased its capabilities in resolving the electrochemical and spectral responses of exfoliated graphene basal plane with varying defect levels [63]. Two contributions, stemming from the intact and defective areas on the surface, respectively, were discovered both in the Raman G band shifts and cyclic voltammetry using the hexaammineruthenium complex. Consequently, two independent electron transfer processes of slower and faster rates coexist in one sample, but they are restricted to the defect-free and defect-rich areas, respectively [63]. This finding is in stark contrast to the previous reports, where the electron transfer processes and the ensuing G band shift rate are dominated by the faster response originating on the defects, either from the flake edges or grain boundaries.

A follow-up study focused on the microscopic effect of electrolyte gating on graphene, as it is arguably one of the most efficient ways to induce a field effect in solid semiconductors and related materials. The field effect is facilitated by the electrical double-layer with a significantly larger capacitance than that in the conventional solid-state dielectric gates. However, the current experimental limits of the electrolyte gating in terms of the highest achievable charge carrier density and dependence of the capacitance on the applied voltage are unknown. We studied the electrostatic gating of monolayer graphene using several high-concentration electrolyte solutions by means of *in-situ* Raman spectroelectrochemistry [64]. Our results showed that the gating efficiency, expressed as the ratio between the Fermi level shift and the applied voltage, was independent of ionic species and concentration, which only influenced the initial doping state of graphene. Theoretical analysis of different gating media showed that the electrolyte gating efficiency reaches ca. 70%, compared to ca. 10% for solid-state alternatives, for typical conditions [64].

5. Conclusions and Outlook

The preceding paragraphs have provided a few glimpses into the capabilities of relatively accessible methods, such as Raman or photoluminescence microspectroscopy, or AFM, for advanced characterization of 2D materials, even in ambient conditions. At the same time, some of the pitfalls have hopefully become apparent. Lateral resolution, as a thread winding through the cases above, is one of the biggest concerns. Even though it is a well-established fact that, in the vast majority of cases, 2D materials can be heterogenously deformed and charge-doped almost on an atomic scale, data obtained with micrometer resolution are still sometimes treated as being perfectly capable of accurately telling the state of the studied 2D specimen. However, in fact, such characterizations must be treated, to some extent, as ensemble measurements. The apparent splitting of the Raman A_1 mode of TMDCs on gold, stemming from the heterogeneous interactions, or the imaginary interlayer exciton in WSe_2-MoS_2 heterobilayers, which, in fact, is just a signal from WSe_2 nanobubbles, belong to two of the most notable examples in my work.

To understand how these spectral features reflect the actual local state of the material, one needs to first conduct experiments where the material's state is changed in a controlled manner. Deformation applied either directly or through stress transferred from a loaded support has to be accompanied by an independent gauge capable of capturing the changes in the specimen. To this end, the works presented in Chapter 4 have helped to set a solid foundation for a quick and accurate determination of graphene's lattice deformation through Raman spectroscopy, which was extended to other carbonaceous materials like carbon fibers, and later to other 2D materials beyond graphene like TMDCs. Such knowledge then enabled us to correctly interpret those previously wrongly assigned PL signals in WSe_2-MoS_2 and pinpoint their true cause: the strain in nanobubbles pressurized from the inside by trapped contamination.

And, *vice versa*, lateral resolution is no less important from the viewpoint of the external perturbation. Electrochemical charge doping (or gating) commences differently through the defect-free basal plane and *via* edges or other defects. Such a distinction would not be possible without a localized probe, like a microdroplet (or smaller), capable of targeting a specific spot on the sample, with or without defects, at will.

However, as stated above, the crystal lattice and optoelectronic structure of 2D materials can fluctuate at the atomic scale. Hence, micrometer or even nanometer resolution might not be sufficient. There is a push to exert changes through nanometer-sized probes and use them simultaneously to monitor those changes in real time.

Tip-enhanced spectroscopy systems enable such experiments. Even though not down to the atomic level in the ambient, combinations of indentation, illumination, photocurrent measurements, Raman and PL measurements, and electrochemistry are possible, and some of them have been tested in our laboratory. Using the same approaches, but without electrochemistry, it is also possible to reach the atomic scale in UHV. In my opinion, only a few other methods can rival the possibilities of concurrently perturbing and scrutinizing so many properties at once with so high lateral resolution, such as tip-enhanced spectroscopy setups.

6. References

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