#### 2.3 High-resolution IETS-STM imaging

The IETS-STM high-resolution technique introduced by W. Ho et al. [10] maps out variations of the IETS signal corresponding to the frustrated translation (FT) mode of the CO-tip while scanning a molecule on the surface in close tip-sample distances. The variation of the IETS signal of FT mode at a low bias set point (typically few meV) traces the chemical structure including characteristic sharp edges very similar to AFM and STM mode. This similarity with the other imaging modes points towards a joint mechanism behind them.

It is well known that a CO molecule placed on the tip or surface has two characteristic well-defined low energy excitation peaks corresponding to the frustrated translation and rotational mode [5]. It is only the frustrated translation mode, which exhibits distinct changes when the CO-tip is approached towards the surface [84]. This is related to the low effective stiffness of the frustrated translational mode which can be consequently modified by the tip-sample interaction. The energy of the frustrated translation vibrational mode of CO-tip was estimated to be  $\approx 2.4$  meV [10], which corresponds to an effective stiffness k = 0.6 N/m; using  $\epsilon = \hbar \sqrt{\frac{k}{m}}$ , where m is the effective mass of the atom/molecule at the tip apex. This value matches very well with values presented by Gross et al. [34]. They estimated the stiffness k of the CO-tip apex experimentally  $\approx 0.5$  N/m and total energy DFT calculations gave values within the range 0.3-1.6 N/m. Weymouth et al. [36] obtained the stiffness k = 0.24 N/m by a thorough analysis of 3D frequency shift vs. distance measurements of a CO-tip interacting with CO on the surface. With the stiffness range of 0.25-0.6 N/m used in PP-AFM [32, 46, 57, 58] and PP-STM [44] simulations one can obtain good agreement with experimental evidence.

To explain the origin of the high-resolution IETS-STM mechanism, we extended the PP-AFM model [32] including analysis of the vibrational modes of the PP [31]. Namely, we employed the standard dynamical matrix approach to evaluate the vibrational energy of the PP for a given tip position. In principle, the PP has three normal modes, where one mode is associated with the radial motion of the PP around the tip apex and two modes reflecting its lateral bending. The first radial mode is relatively stiff and it is not relevant for the analysis of the IETS signal. Nevertheless, the two other modes are much softer and they can be directly associated to the frustrated translation mode of a CO-tip. In the IETS-STM model, the vibrational energy of the lateral PP modes is set to be  $\approx 2 \text{ meV}$  for a free standing PP, which corresponds to the lateral PP stiffness k = 0.6 N/m. However, the FT vibrational energy varies during scanning due to the tip-sample interaction. Namely, the attractive (convex) and repulsive (concave) character of the surface potential induces vibration mode hardening and softening, respectively, as shown in Figure 2.9(a,b).

Our model [31] convincingly showed that the IETS mechanism is related to a variation of the frustrated translational mode of a CO molecule placed at the tip apex, which responds sensitively to the changes of a local curvature of the surface potential. To explain the imaging IETS-STM mechanism in more details, let us consider a simple example depicted on Figure 2.9(c). In this scenario, the PP is scanned across a bond/atom at a certain height. When located far from the atom/bond the FT vibrational energy remains unaltered because of negligible interaction of the PP with the substrate. However, when the PP is located above the bond/atom, its FT energy is consequently reduced by experiencing the repulsive interaction with the substrate. The IETS signal detected at a given bias set point is enhanced as shown in Figure



Figure 2.9: Explanation the origin of the IETS-STM contrast obtained with functionalized tips. (a) Interaction energies of the probe particle for different tipsample distances consisting of  $V_{SPRING}$  (solid line) and varying  $V_{ATOM}$  (dashed line) for different positions above an atom on surface. (b) Variation of FT vibrational mode (red line) and the interaction energy with surface atom ( $V_{ATOM}$ ; black line) with tipsample distance. (c) Evolution of IETS-STM signal across a surface atom due to renormalisation of the energy of the FT vibrational mode (red line). (d) correlation between the bending of the probe particle and the contrast in AFM, STM and IETS-STM images calculated for different tip-sample distances. (Adopted from [31]).

2.9(c). Thus the renormalisation of FT modes of CO on the tip [84] and the consequent variation of the IETS signal gives rise to the characteristic contrast observed in high-resolution IETS-STM images.

We should note that the model explains only the contrast using the variation of the FT vibrational energy, but completely omits the intensity of the IETS signal. However detailed inspection of the experimental data reveals that the variation of the intensity also contributes to the high-resolution IETS-STM contrast. Nevertheless, understanding of this phenomenon requires more sophisticated theoretical approaches. Currently, we are developing a new model to address the variation of the intensity of the IETS signal, which takes into account modulation of the tunneling matrix with respect to the FT vibrational mode.

It is interesting to compare high-resolution images of all the techniques calculated with the PP model [31]. Figure 2.9(d) displays simultaneously calculated highresolution AFM, STM and IETS-STM images together with lateral bending of the PP position at different tip-sample distances. This comparison demonstrates that the sharpening of sub-molecular contrast is closely related to the lateral bending of the CO-probe in the repulsive regime. It also puts the IETS-STM imagining mechanism on common ground with already established high-resolution AFM and STM mechanisms [31]. However direct experimental evidence correlating the AFM/STM/IETS imaging mechanisms has been missing so far. Vert recently, we have succeeded to acquire simultaneous high resolution AFM/STM/IETS imaging of iron(II) phthalo-



Figure 2.10: Simultaneous high-resolution AFM, STM and IETS-STM images of FePc on Au(111) surface acquired with CO-tip. The images were recorded using standard LT-SPM Createc machine equipped with qPlus sensor at 4 Kelvin with amplitude A = 50 pm and bias voltage 3 mV.

cyanine (FePc) on Au(111) surface with CO-functionalized probe, as shown on Figure 2.10. The acquired data demonstrate unambiguously the common imaging mechanism of the modes. We show that not only renormalization of the frustrated translational mode, but also variation of the amplitude of IETS signal affect the IETS imaging.

#### 2.4 Imaging charge distribution within molecules

The electrostatic field of molecules largely determines its behaviour, e.g. it affects preferred sites within the molecule, where chemical reactions with other compounds can take a place. It is also crucial to understand self-assembling processes of individual molecules forming e.g. supramolecules or determining the electron-hole pair dynamics in excited states. Detailed resolution of the charge distribution in the chemical bonds within a molecule significantly advances our current possibilities to study the charge transfer at the atomic and molecular level. For example, the detailed knowledge of the charge distribution on molecular level could help to design solar cells with better functionality.

#### 2.4.1 Kelvin probe force spectroscopy

The mapping of the electrostatic field in real space is an important task for scanning force microscopy, which is still not satisfactorily resolved. Kelvin Probe Force Microscopy (KPFM) has been so far a widely used technique, which enables the mapping of the local contact potential difference (LCPD) [6] on atomic [85, 86] and molecular scale [87, 88, 89]. It was shown that the KPFM contrast can be substantially enhanced using functionalized probes [87, 61]. Nevertheless, the traditional KPFM method suffers from an unclear relation between the detected signal (LCPD) and the quantities of interest (charge distribution, electrostatic field). Furthermore, we demonstrated that



Figure 2.11: Sub molecular resolution of charge densities of molecules by means of KPFS method. a) Atomically resolved atomic force microscope image of molecules, trimeric perfluoroortho-phenylenemercury ( $F_{12}C_{18}Hg_3$ ) and its hydrogenterminated counterpart ( $H_{12}C_{18}Hg_3$ ) on the surface of Cu (111). (b) The charge distribution simulated using quantum mechanical calculations. (c) Image of the submolecular charge distribution of the studied molecules obtained by the new KPFS method showing the different polarity of the chemical C-H and C-F bonds, respectively.

the proximity of the scanning probe near the surface induces undesired artifacts in KPFM measurements [90]. These give rise to spurious alteration of the measured signal [90]. Namely, reaching submolecular spatial resolution of KPFM signal is possible only in the very close distance regime, where the acquired signal is governed by the complex interplay of local electrostatic fields of tip and sample, their polarization, the bending of the probe and the presence of conductance through the tunnelling junction. This prevents precise determination of the charge distribution within a single molecule with the traditional KPFM technique.

Therefore there is strong demand to establish a new technique, which overcomes, at least partially, the drawbacks of the KPFM technique. We introduced an alternative measuring protocol that allows removal of the aforementioned artifacts of KPFM [90]. The method of detecting charge distribution, which is based on measuring the Kelvin probe force spectroscopy (KPFS) for two different voltages applied to the scanning probe. Namely, we investigated trimeric perfluoroortho-phenylenemercury ( $F_{12}C_{18}Hg_3$ ) and its derivate, which contains hydrogen instead of fluorine atoms ( $H_{12}C_{18}Hg_3$ ) on periphery of the molecule. Consequently, different electronegativity of hydrogen (H) or fluorine (F) gives rise to different bond polarization between carbon and hydrogen atoms (C-H) and fluorine (C-F), respectively, as shown on Figure 2.11.

#### 2.4.2 Mapping the electrostatic potential from image distortions

Recently, we introduced a new method [46], which exploits deformations occurring in the high-resolution AFM/STM images due to the electrostatic interaction, as depicted schematically on Figure 2.5. It has clear theoretical interpretation at the very close distance required to achieve sub molecular resolution. Furthermore, the method enables simultaneous acquisition of the electrostatic field together with information about the chemical structure of the inspected molecule, as shown on Figure 2.12.



Figure 2.12: Determining the electrostatic field above a close-packed PTCDA layer. (a,b) experimental high-resolution AFM images of a self-assembled monolayer of PTCDA deposited on Ag(111) obtained with two different Xe tips. (c) simulated AFM image using an effective charge Q = 0.0 e and the effective lateral stiffness  $k = 0.16 \text{ Nm}^{-1}$ . (d) same as (c), but with Q = +0.3 e and  $k = 0.20 \text{ Nm}^{-1}$ . (e,f) the experimental images superimposed with a deformation grid defined by comparing the corresponding sharp features between the two images in (a) and (b). (g) electrostatic potential calculated from the deformation field (grey arrows). (h) calculated Hartree potential from DFT simulations 3.0 Å above the molecular layer.

The new method can determine the electrostatic field on a single molecule from distortions of high-resolution images acquired with scanning probes. In this particular case, the outermost atom/molecule of the probe is significantly displaced during scanning by the electrostatic field of the probed molecules, very similar to an arm of the classical electroscope. Consequently, the movement of the front atom on the probe induces the distortions of the positions of atoms and bonds seen in the high-resolution images taken by means of AFM, like the deformation of images of stars and galaxies in astronomical photographs due to the strong gravitational field (i.e. the Einstein gravitational lensing). We employed the degree of the observed deformation to the reconstructing the electrostatic field in the vicinity of the investigated molecules, as shown on Figure 2.12.

The method provides certain advantages over KPFM method, improving substantially the spatial resolution of the detected electrostatic field. Moreover, the method enables us to obtain simultaneously the electrostatic field together with information on the chemical structure of the inspected molecule. Moreover, the principle of the method may be utilised in the future for mapping other force fields around molecules, such as magnetic fields. On the other hand, it relies on the presence of the sharp edges, which limits the resolution outside of single molecules.

#### 2.5 Tracking on-surface chemical reactions

Despite the advances of the on-surface chemistry to form molecular assemblies (see e.g. [91, 92, 93, 94], detailed understanding of elementary reaction steps including identification of intermediates and final chemical products has been a challenge for many years. This situation dramatically changed with the invention of high-resolution SPM imaging. In their seminal work, D. de Oteyza et al. [26] demonstrated that individual reactants, intermediates and final products of thermally induced enediyne cyclization reactions can be identified with unprecedented resolution. This provides the unique insight into pathways of on-surface chemical reactions, which cannot be achieved by other techniques. This breakthrough initiated large activities in studying chemical reactions on both metal and insulator surfaces. For example, it allowed the study of the reversible generation of individual polycyclic aryne molecules [24] or covalent fusion of tetrapyrroles to graphene edges [95]. We performed combined experimental and theoretical study of regioselectivity in formation of organometallic complexes [96].

The technique also became invaluable in characterization of growth processes of graphene nanoribbons [97, 98, 99, 100, 101] or other 2D materials [102], supramolecular structures [89, 53] or covalent networks [103].

#### 2.5.1 Self-assembling of ferrocene derivates on different surfaces



Figure 2.13: Different adsorption of FcDA molecules on various surfaces Constant height AFM images of 1,1'-ferrocene dicarboxylic acid (FcDA) molecules on different Ag(111), Cu(110) and Cu<sub>3</sub>N/Cu(110) substrates.

Ferrocene-based molecules are extremely appealing as they offer a prospect of having built-in spin or charge functionality. However, there are only limited number of studies of the structural and electronic properties on surfaces so far. We investigated the self-assembly processes of 1,1'-ferrocene dicarboxylic acid (FcDA) molecules ( $C_{12}H_{10}FeO_4$ ) on both metallic (Ag(111), Au(111), Cu(110)) and insulating (Cu<sub>3</sub>N/Cu(110)) surfaces with high-resolution nc-AFM/STM, XPS and NEXAFS [104]. The experimental evidence is corroborated with total energy DFT calculations and nc-AFM simulations. We found very different behavior of FcDA molecules on noble metal (Ag,Au) and Cu-based surfaces. On the Ag(111) and Au(111) surfaces, the FcDA molecules interacts weakly with the substrate forming a complex self-assembled pattern. We were able to determine the molecular arrangement of the self-assembled molecular layer, see Figure 2.13, combining the high-resolution nc-AFM images with CO-decorated tip, total energy DFT calculation and the simulation of nc-AFM images.

In the case of Cu(110) and Cu<sub>3</sub>N/Cu(110) surfaces, FcDA molecules undergo a dehydrogenation of carboxylic groups. As a consequence, the FcDA are strongly bound to the substrate via oxygen atoms. On Cu(110), the FcDA molecules tend to organize into relatively dense islands with internal disorder. The character of this structure reveals surface-mediated attractive interaction between the molecules. On the other hand, we observe mostly random distribution of FcDA molecules on the Cu<sub>3</sub>N/Cu(110) surfaces. Our study indicates that the FcDA adsorption takes place most likely on Cu atoms residing near the native N-vacancies present in the Cu<sub>3</sub>N/Cu(110) layer. Thus our study indicates that the Cu in general has critical influence on the stability of the carboxylic group.

#### 2.5.2 Resolving transformations of molecules and their chirality on surfaces



Figure 2.14: Schematic view of the chirality-preserving transformation of molecules deposited on a solid surface (A) using a temperature-controlled chemical reaction ( $T_1$ ). This reaction allows to get the same chirality of adsorbed molecules across the whole monolayer (green frame). Importantly, this chiral arrangement cannot be reached by simple deposition of the prochiral molecules onto the surface (B and C).

Chirality is a geometrical property of an object (usually a molecule or ion) that cannot be matched with its mirror image. Chirality plays a key role in nature and can be demonstrated for example on the relationship of right and left hand, which are not identical in terms of symmetry. The phenomenon of chirality is important in many areas e.g. stereoselective reactions, self-assembly of molecules, biological processes (where proteins, nucleic acids or polysacharides are involved), the polarization of light or electron spin. Control of chirality in chemical reactions in solutions represents one of the greatest achievements of organic chemistry in the last fifty years. Molecules that are not chiral in solution or gas phase (i.e. prochiral), may become chiral under certain conditions, specifically after adsorption to a solid surface, when a so-called chiral adsorbate is formed. The whole array of such molecular adsorbates is naturally racemic as spontaneous global mirror-symmetry breaking is disfavored, as shown schematically on Figure 2.14. In our recent work, we demonstrated a chemical method of obtaining flat prochiral molecules adsorbed on the solid achiral surface in such a way that one adsorbate handedness globally dominates. We observed a chemical transformation of individual molecules on silver surface and demonstrated chirality transfer during the reaction [27]. We employed the high-resolution AFM imaging, which allows us to determine their molecular structure and the chirality. We have proven the possibility to prepare an extensive two-dimensional molecular layer of chosen chirality. This achievement represents the first practical demonstration of the possibility that prochiral molecules at solid surfaces occupy either right or left-handed orientation on purpose.



Figure 2.15: Determination of intermediates and final products of the chemical reaction. Molecular structures of polyaromatic molecules obtained during different stages of the chemical transformation on a crystalline silver surface (a-c). The accurate determination of the chemical structure of the individual products was carried out using scanning probe microscopes with high spatial resolution (d-k,l-o). The cascade of chemical reactions transforming the initial helicene molecules (DBH) into various intermediates and final products is schematically illustrated in (p).

Namely, we achieved that the adsorbed molecules adopted a single chirality in their whole monolayer, by using a thermally controlled chemical transformation of chiral helical molecules, so-called helicenes, to planar polyaromatic molecules (see Figure 2.14). The transformation was made on a surface of a silver crystal. Moreover, we could accurately determine a sequence of multi-step chemical transformations of the molecules using atomic force microscope that operates at temperatures close to the absolute zero and under conditions of ultra-high vacuum. We managed to identify both intermediates and final products of the cascade of chemical reactions, employing the unique submolecular resolution that allowed the direct deduction of the molecular structures of the relevant molecules (see Figure 2.15).

This work represents a novel approach enabling in-depth studies of chemical reactions on solid state surfaces and a precise determination of the chemical structure of molecules, with the possibility to track conversions of their chirality. The original method opens up new possibilities for the preparation of well-defined chiral surfaces that have significant potential for use in the field of heterogeneous catalysis, sensors of chirality, molecular electronics, spintronics, photonics and biochemistry.

# 2.6 Measuring weak interactions and the electron transport between molecules

The possibility to decorate a molecule or noble gas atom on tip apex may not only serve for obtaining high resolution, but can be used to study the interaction between selected functional groups of molecules or individual atoms. Indeed this possibility was recognised very early by P. Liljeroth and colleagues [28], who performed force spectroscopy measurements between two CO molecules, placed on the surface and tip, respectively. The force spectroscopy measurements [48] provide direct access to interaction energies between two outermost atoms/molecules located on surface and tip as a function of the distance between the studied objects. This kind of information is hardly accessible by other experimental techniques. Thus it opens completely new perspectives to study weakly interacting systems and to establish well-defined benchmarks for theoretical methods describing the weak interactions. Several new studies including experimental and theoretical measurements have appeared recently [105, 29, 30].

The force spectroscopy technique can be easily extended into 3D force volume mapping [106, 107, 108], where the spectroscopy curves are measured systematically on a pre-defined grid on the surface. The 3D-mapping procedure is able to provide detailed spatial variation of the interaction force between tip and sample [109]. From this perspective, it can analyse not only strength but also directionality of the bond established between tip and sample. It has been shown that 3D force spectroscopy with functionalized tips may provide the interaction potential between the molecule at the tip and the one at the sample [28, 36]. Combining the species-specific selectivity of the custom designed tips with the ability to quantify tip-sample interactions with site-specific accuracy opens new opportunities for the study of the non covalent bonding mechanism between two constituents in a very controlled way.

## 2.6.1 Formation of molecular contacts: AFM/STM and DFT study

We carried out combined experimental and theoretical study the forces between two single molecules brought into contact, and their connection with charge transport through the molecular junction using non contact AFM, STM, and DFT simulations [29]. A carbon monoxide molecule approached to an acetylene molecule  $(C_2H_2)$  feels initially weak attractive electrostatic forces, partly arising from charge reorganization in the presence of molecular dipoles located on molecule on tip and surface, respectively. The electrical polarization of the molecules rises as they are brought into contact, leading to a gradual increase in the local contact potential difference. We found that the molecular contact is chemically passive, and protects the electron tunneling barrier from collapsing, even in the limit of repulsive forces. In the close distances, repulsive forces cause the bending of the CO molecule and the decrease of the stiffness of the junction. In addition, the lateral bending of the CO molecule on tip modifies significantly transmission channels within the tunnelling junction. We also identified subtle conductance and force variations at different contacting sites along the  $C_2H_2$  molecule attributed to a weak overlap of their respective frontier orbitals.



Figure 2.16: Process of picking up CO molecule form Ag(111) surface to tip apex (a) STM constant-current topography image (sample bias  $V_{bias} = 5mV$ , tunnelling current  $I_t = 10$  pA) of CO on Ag(111) taken with a non functionalized tip. (b) STM constant-current topography image ( $V_{bias} = 5 \text{ mV}$ ,  $I_t = 10$  pA) after picking up a single CO atom by approaching the tip towards the CO molecule which was located at the position identifed by a dotted circle. c) Characteristic AFM contrast after placing CO on the tip apex.

#### 2.6.2 Interaction between CO-CO molecules

Proper theoretical description of the weak vdW interaction, despite the large effort, still remains elusive and is intensely investigated. We intentionally prepared and investigated the interaction between two CO molecules deposited on Ag(111) surface and tip apex by a high-resolution 3D mapping and molecular manipulation with the AFM technique, see Figure 2.16. We determined the interaction energies using high-resolution AFM imaging and compared them to the total energy DFT-vdW calculations.

We used the force-distance spectroscopy data, acquired with functionalized CO-tips, to gain direct access to the weak interaction forces acting between the functionalized tips and CO molecules on surface. Such information provides a unique opportunity to benchmark the available theoretical methods employed to describe the vdW interaction. We compared directly various vdW methods to the experimental energy vs. distance data. First we analysed reproducibility of the measurement and showing the size of error we have during measurement. Namely, we analyzed in detail the interaction energy between two CO molecules. To do that, we acquired several force-distance spectroscopy taken with different CO-terminated tip above a single CO molecule absorbed on the Ag(111) surface to get reliable statistics. We found that the average binding energy is about 0.27 kcal/mol, varying between 0.21 kcal/mol and 0.38 kcal/mol ac-

cording to CO-terminated tips. The direct access to the interaction energies between two well defined CO molecules, gives us the unique opportunity to benchmark different vdW-functionals. Thus we can compare the total energy DFT calculations using different vdW approximations [110, 111, 112, 113] against the available experimental data as summarized on Figure 2.17.



Figure 2.17: Experimental and theoretical interaction energies between two CO molecules placed on Ag(111) surface and metallic tip apex, respectively. a) Variation of the interaction energy of the same CO-tip with different CO molecules deposited on Ag(111) surface; b) Variation of the interaction energy between different CO-tips and CO-molecules on Ag(111) surface; c) Comparison of an average experimental interaction energy (evaluated from b)) with calculated total energies vs. distance using different DFT-vdW functionals [110, 111, 112, 113].

So far, this technique has been applied to previously established systems such as noble gases (Xe, Kr) or CO molecules. With a bit of ambition, one can think about direct measurement of different kinds of non covalent interactions, such as hydrogen,  $\pi$  or halogen bonds. For example halogen chalcogen, and pnictogen bonds are now subject to intensive research in chemistry, but our understanding relies mostly on sophisticated but computationally demanding quantum chemistry methods. The possibility to directly measure interaction energy of selected functional groups with the  $\sigma$ -hole of a halogen atom, or even better to directly image the  $\sigma$ -hole by a functionalized tip, represents an invaluable source of information, and also may establish solid benchmarks for the high-level theories.

The hydrogen bond is another class of non-covalent bond of ita existence, which again becomes the center of recent interest to scientists for its importance in biological systems. After nearly 100 years of existence, the hydrogen bonds got a new definition [114], which reflects these new developments and insights. From this perspective, the possibility to directly measure not only its strength but also directionality of non covalent bonds could bring more valuable information about their behaviour.

The main obstacle in the cases discussed above is not in the measurements, but rather a more suitable design of functional groups/molecules We need not only molecules which remain stable upon deposition in UHV environment, but that can also adopt the most favorable mutual orientation when placed on tip and surface. Apparently, this task requires close cooperation with gifted chemists.

## Chapter 3 Conclusion and Outlook

In conclusions, we advanced substantially our understanding of the mechanism of high resolution imaging with functionalized tips. We devised robust theoretical description of the high-resolution atomic force microscopy (AFM) scanning probe microscopy (STM) and inelastic electron tunnelling spectroscopy (IETS) imaging, which not only explains the contrast but it also provides an efficient modelling tool of AFM [32, 31, 57, 46], STM [32, 44] and IETS-STM [31] images. We developed a simulation package, which is freely available on internet and used by many groups around the world nowadays [39]. In addition, we mastered experimentally the high-resolution SPM imaging with different functionalized tips. This allowed us to study e.g. novel chemical reactions on surfaces [27] or measure weak vdW interaction between individual molecules (carbon monoxide) or noble gases (Xe). For the first time, simultaneously AFM/STM/IETS-STM images of molecules with sub molecular resolution were acquired. This opens new possibilities for complex characterization of molecular systems including chemical identification. A new method that allows one to achieve sub-molecular resolution even at room temperature with standard tips was presented [67]. Two new methods, which allow mapping charge distribution within molecules on surfaces with unprecedented spatial resolution, were developed. The first method allows us to resolve the polarity of individual chemical bonds in a single molecule [90]. The second method determines the electrostatic field on a single molecule from distortions of high-resolution images acquired with scanning probes [46]. We demonstrated that the elements within an organic molecule can be discriminated on the atomic level by acquiring 3D frequency shift data with a carbon monoxide terminated tip, combined with DFT and molecular mechanics calculations [58]. We studied a chemical transformation of individual molecules on a metal surface [96] and demonstrated chirality transfer during the reaction [27].

The invention of high-resolution imaging techniques has initiated novel research lines and substantially advanced our possibilities to characterise molecules and nanostructures on surfaces under UHV conditions with the unprecedented spatial resolution. The detailed understanding of the underlying imaging mechanisms has allowed their exploitation providing new possibilities not only for imaging chemical structure of single molecules on surfaces but also to obtain valuable information about their chemical and physical properties. Nowadays the basic mechanism of the high-resolution AFM/STM and IETS-STM images is fairly well understood. Furthermore, the underlying mechanism can be adopted to explain enhanced contrast observed in other scanning probe modes such as contact STM, liquid nc-AFM or electrochemical STM. These days, the high-resolution AFM/STM techniques are well established and adopted by many research groups around the world. Many groups have mastered these techniques providing many exciting results in different fields. Several challenges remain open, such as spin resolution, chemical sensitivity, imaging complex non planar molecules etc. Nevertheless, these techniques have boosted new research lines, which were unimaginable before their development in just the last decade. In just this short period, it has become not only an indispensable tool in solving critical problems of fundamental science, but has also found industrial applications. Therefore we can expect many new discoveries and surprises, as yet unforeseen today.

### Bibliography

- G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel. Surface Studies by Scanning Tunneling Microscopy. *Physical Review Letters*, 49:57–61, 1982.
- [2] G. Binnig and C. F. Quate. Atomic Force Microscope. *Physical Review Letters*, 56:930–933, 1986.
- [3] S. Morita, R. Wiesendanger, and E. Meyer, editors. Noncontact Atomic Force Microscopy vol. 1. Springer Berlin Heidelberg, Berlin Heidelberg, 2002.
- [4] S. Morita, F.J. Giessibl, and R. Wiesendanger, editors. Noncontact Atomic Force Microscopy vol. 2. Springer-Verlag Berlin Heidelberg, Berlin Heidelberg, 2009.
- [5] B.C. Stipe, M.A. Rezaei, and W. Ho. Single-Molecule Vibrational Spectroscopy and Microscopy. *Science*, 280:1732–1735, 1998.
- [6] S. Sadewasser and Th. Glatzel, editors. Kelvin Probe Force Microscopy: Measuring and Compensating Electrostatic Forces. Springer-Verlag Berlin Heidelberg, Berlin Heidelberg, 2012.
- [7] F. J. Giessibl. High-speed force sensor for force microscopy and profilometry utilizing a quartz tuning fork. *Applied Physics Letters*, 73:3956–3958, 1998.
- [8] R. Temirov, S. Soubatch, O. Neucheva, A.C. Lassise, and F.S. Tautz. A novel method achieving ultra-high geometrical resolution in scanning tunnelling microscopy. *New Journal of Physics*, 10:053012, 2008.
- [9] L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer. The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy. *Science*, 325:1110–1114, 2009.
- [10] C. Chiang, C. Xu, Z. Han, and W. Ho. Real-space imaging of molecular structure and chemical bonding by single-molecule inelastic tunneling probe. *Science*, 344:885–888, 2014.
- [11] A Gewirth and Brian K. Niece. Electrochemical Applications of in Situ Scanning Probe Microscopy. Chem. Rev., 97:1129–1162, 1997.
- [12] J.A. Stroscio and R.J. Celotta. Controlling the dynamics of a single atom in lateral atom manipulation. *Science*, 306:242–7, 2004.
- [13] Y.-H. Zhang, P. Wahl, and K. Kern. Quantum point contact microscopy. Nano letters, 11:3838–43, 2011.
- [14] G. Schull, Y.J. Dappe, C. G., H. Bulou, and R. Berndt. Charge injection through single and double carbon bonds. *Nano letters*, 11:3142–6, 2011.

- [15] S. Ido, H. Kimiya, K. Kobayashi, H. Kominami, K. Matsushige, and H. Yamada. Immunoactive two-dimensional self-assembly of monoclonal antibodies in aqueous solution revealed by atomic force microscopy. *Nature Nanotechnology*, 13:264–270, 2014.
- [16] T. Fukuma, K. Kobayashi, K. Matsushige, and H. Yamada. True atomic resolution in liquid by frequency-modulation atomic force microscopy. *Applied Physics Letters*, 87:034101, 2005.
- [17] J. Repp, G. Meyer, S. Stojković, A. Gourdon, and Ch. Joachim. Molecules on Insulating Films: Scanning-Tunneling Microscopy Imaging of Individual Molecular Orbitals. *Physical Review Letters*, 94:026803, 2005.
- [18] L. Gross, N. Moll, F. Mohn, A. Curioni, G. Meyer, F. Hanke, and M. Persson. High-Resolution Molecular Orbital Imaging Using a p-Wave STM Tip. *Physical Review Letters*, 107, 2011.
- [19] Ch. Weiss, Ch. Wagner, C. Kleimann, M. Rohlfing, S.F. Tautz, and R. Temirov. Imaging Pauli Repulsion in Scanning Tunneling Microscopy. *Physical Review Letters*, 105:086103, 2010.
- [20] Ch. Weiss, Ch. Wagner, R. Temirov, and F.S. Tautz. Direct Imaging of Intermolecular Bonds in Scanning Tunneling Microscopy. *Journal of the American Chemical Society*, 132:11864–11865, 2010.
- [21] L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, and G. Ertl. Dynamics of Electron-Induced Manipulation of Individual CO Molecules on Cu(111). *Phys. Rev. Lett.*, 80:2004–02007, 1998.
- [22] S. Morita, F.J. Giessibl, E. Meyer, and R. Wiesendanger, editors. *Noncontact Atomic Force Microscopy vol. 3.* Springer International Publishing, Berlin, 2015.
- [23] L. Gross, N. Moll, G. Meyer, R. Ebel, W.M. Abdel-Mageed, and M. Jaspars. Organic Structure Determination Using Atomic-resolution Scanning Probe Microscopy. *Nature Chem.*, 2:821–825, 2010.
- [24] N. Pavliček, B. Schuler, S. Collazos, N. Moll, D. Perez, E. Guitin, G. Meyer, D. Pena, and L. Gross. On-surface generation and imaging of arynes by atomic force microscopy. *Nature Chem.*, 7:623–628, 2015.
- [25] B. Schuler, G. Meyer, D. Pena, O.C. Mullins, and L. Gross. Unraveling the Molecular Structures of Asphaltenes by Atomic Force Microscopy. *Journal of* the American Chemical Society, 137:9870–9876, 2015.
- [26] D.G. de Oteyza, P. Gorman, Y.-Ch. Chen, S. Wickenburg, A. Riss, D.J. Mowbray, G. Etkin, Z. Pedramrazi, H.-Z. Tsai, A. Rubio, M.F. Crommie, and F.R. Fischer. Direct imaging of covalent bond structure in single-molecule chemical reactions. *Science*, 340:1434–1437, 2013.
- [27] O. Stetsovych, M. Švec, J. Vacek, J. Vacek Chocholoušová, A. Jančařík, J. Rybáček, K. Kosmider, I. G. Stará, P. Jelínek, and Starý I. From helical to planar chirality by on-surface chemistry. *Nature Chemistry*, 9:213–218, 2017.

- [28] Zh. Sun, M. Boneschanscher, I. Swart, D. Vanmaekelbergh, and P. Liljeroth. Quantitative Atomic Force Microscopy with Carbon Monoxide Terminated Tips. *Physical Review Letters*, 106:046104, 2011.
- [29] M. Corso, M. Ondracek, Ch. Lotze, P. Hapala, K.J. Franke, P. Jelínek, and J.I. Pascual. Charge Redistribution and Transport in Molecular Contacts. *Physical Review Letters*, 115:136101, 2015.
- [30] Sh. Kawai, A.S. Foster, T. Björkman, S. Nowakowska, J. Björk, F.F. Canova, L.H. Gade, Th.A. Jung, and E. Meyer. Van der Waals interactions and the limits of isolated atom models at interfaces. *Nature Communications*, 7:11559, 2016.
- [31] P. Hapala, R. Temirov, F.S. Tautz, and P. Jelínek. Origin of High-Resolution IETS-STM Images of Organic Molecules with Functionalized Tips. *Physical Re*view Letters, 113:226101, 2014.
- [32] P. Hapala, G. Kichin, Ch. Wagner, F.S. Tautz, R. Temirov, and P. Jelínek. Mechanism of high-resolution STM/AFM imaging with functionalized tips. *Physical Review B*, 90:085421, 2014.
- [33] N. Moll, L. Gross, F. Mohn, A. Curioni, and G. Meyer. The mechanisms underlying the enhanced resolution of atomic force microscopy with functionalized tips. *New Journal of Physics*, 12:125020, 2010.
- [34] L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitian, D. Pena, A. Gourdon, and G. Meyer. Bond-Order Discrimination by Atomic Force Microscopy. *Science*, 337:1326–1329, 2012.
- [35] J. Welker and F.J. Giessibl. Revealing the Angular Symmetry of Chemical Bonds by Atomic Force Microscopy. *Science*, 336:444–449, 2012.
- [36] A.J. Weymouth, T. Hofmann, and F.J. Giessibl. Quantifying Molecular Stiffness and Interaction with Lateral Force Microscopy. *Science*, 343:1120–1122, 2014.
- [37] M. Neu, N. Moll, L. Gross, G. Meyer, F.J. Giessibl, and J. Repp. Image correction for atomic force microscopy images with functionalized tips. *Physical Review B*, 89:205407, 2014.
- [38] S.K. Hämäläinen, N. van der Heijden, J. van der Lit, S. den Hartog, P. Liljeroth, and I. Swart. Intermolecular Contrast in Atomic Force Microscopy Images without Intermolecular Bonds. *Physical Review Letters*, 113:186102, 2014.
- [39] the probe particle model is available online on http://nanosurf.fzu.cz/ppr/.
- [40] M. Ellner, N. Pavliček, P. Pou, B. Schuler, N. Moll, G. Meyer, L. Gross, and R. Perez. The Electric Field of CO Tips and Its Relevance for Atomic Force Microscopy. *Nano Letters*, 16:1974–1980, 2016.
- [41] M.A. Guo, Ch-Sh.and Van Hove, X. Ren, and Y. Zhao. High-Resolution Model for Noncontact Atomic Force Microscopy with a Flexible Molecule on the Tip Apex. Journal of Physical Chemistry C, 119:1483–1488, 2015.

- [42] Y. Sakai, A.J. Lee, and J.R. Chelikowsky. First-Principles Atomic Force Microscopy Image Simulations with Density Embedding Theory. *Nano Letters*, 16:3242–3246, 2016.
- [43] J. Martínez, E. Abad, C. González, F. Flores, and J. Ortega. Improvement of Scanning Tunneling Microscopy Resolution with H-Sensitized Tips. *Physical Review Letters*, 108:246102, 2012.
- [44] O. Krejči, P. Hapala, M. Ondráček, and P. Jelínek. Mapping the electrostatic force field of single molecules from high-resolution scanning probe images. *Phys. Rev. B*, 95:045407, 2017.
- [45] P. Hapala, M. M. Ondráček, O. Stetsovych, M. Svec, and P. Jelínek. Simultaneous nc-AFM/STM measurements with atomic resolution, chapter 3, pages 29–49. Springer International Publishing, Berlin, 2015.
- [46] P. Hapala, M. Svec, O. Stetsovych, N.J. van der Heijden, M. Ondracek, J. van der Lit, P. Mutombo, I. Swart, and P. Jelínek. Mapping the electrostatic force field of single molecules from high-resolution scanning probe images. *Nature Communications*, 7:11560, 2016.
- [47] R. Pérez, M.C. Payne, I. Stich, and K. Terakura. Role of covalent tip-surface interactions in noncontact atomic force microscopy on reactive surfaces. *Physical Review Letters*, 78:678–681, 1997.
- [48] M.A. Lantz, H.J. Hug, R. Hoffmann, P.J.A. van Schendel, P. Kappenberger, S. Martin, A. Baratoff, and H.-J. Güntherodt. Quantitative Measurement of Short–Range Chemical Bonding Forces. *Science*, 291:2580–2583, 2001.
- [49] N. Pavliček, C. Herranz-Lancho, B. Fleury, M. Neu, J. Niedenführ, M. Ruben, and J. Repp. High-resolution scanning tunneling and atomic force microscopy of stereochemically resolved dibenzo[a,h]thianthrene molecules. *Physica Status Solidi* (B), 250:2424–2430, 2013.
- [50] J. Zhang, P. Chen, B. Yuan, W. Ji, Z. Cheng, and X. Qiu. Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy. *Science*, 342:611–614, 2013.
- [51] A.M. Sweetman, S.P. Jarvis, H. Sang, I. Lekkas, P. Rahe, Y. Wang, J. Wang, N.R. Champness, L. Kantorovich, and P. Moriarty. Mapping the force field of a hydrogen-bonded assembly. *Nature Communications*, 5:3931, 2014.
- [52] Ch.-Sh. Guo, X. Xin, M.A. Van Hove, X. Ren, and Y. Zhao. Origin of the Contrast Interpreted as Intermolecular and Intramolecular Bonds in Atomic Force Microscopy Images. *The Journal of Physical Chemistry C*, 119:14195–14200, 2015.
- [53] Sh. Kawai, A. Sadeghi, F. Xu, L. Peng, A. Orita, J. Otera, S. Goedecker, and E. Meyer. Extended Halogen Bonding between Fully Fluorinated Aromatic Molecules. ACS Nano, 9, 2015.
- [54] A. Sweetman, S.P. Jarvis, Ph. Rahe, N.R. Champness, L. Kantorovich, and Ph. Moriarty. Intramolecular bonds resolved on a semiconductor surface. *Physical Review B*, 90:165425, 2014.

- [55] J. Guo, J.T. Lu, Y. Feng, J. Chen, J. Peng, Z. Lin, X. Meng, Z. Wang, X.Z. Li, E.G. Wang, and Y. Jiang. Nuclear quantum effects of hydrogen bonds probed by tip-enhanced inelastic electron tunneling. *Science*, 352:321–325, 2016.
- [56] N. Moll, B. Schuler, Sh. Kawai, F. Xu, L. Peng, A. Orita, J. Otera, A. Curioni, M. Neu, J. Repp, G. Meyer, and L. Gross. Image Distortions of a Partially Fluorinated Hydrocarbon Molecule in Atomic Force Microscopy with Carbon Monoxide Terminated Tips. *Nano Letters*, 14:6127–6131, 2014.
- [57] J. van der Lit, F. Di Cicco, P. Hapala, P. Jelínek, and I. Swart. Submolecular Resolution Imaging of Molecules by Atomic Force Microscopy: The Influence of the Electrostatic Force. *Physical Review Letters*, 116:096102–5, 2016.
- [58] N.J. van der Heijden, P. Hapala, J.A. Rombouts, J. van der Lit, D. Smith, P. Mutombo, M. Švec, P. Jelínek, and I. Swart. Characteristic Contrast in  $\Delta$ f<sub>min</sub> Maps of Organic Molecules Using Atomic Force Microscopy. *ACS Nano*, 10:8517–8525, 2016.
- [59] J. Peng, J. Guo, P. Hapala, D. Cao, M. Ondráček, B. Cheng, L. Xu, P. Jelínek, E. Wang, and Y. Jiang. Submolecular-resolution non-invasive imaging of interfacial water with atomic force microscopy. submitted.
- [60] G. Kichin, Ch. Weiss, Ch. Wagner, F.S. Tautz, and R. Temirov. Single Molecule and Single Atom Sensors for Atomic Resolution Imaging of Chemically Complex Surfaces. *Journal of the American Chemical Society*, 133:16847–16851, 2011.
- [61] F. Mohn, B. Schuler, L. Gross, and G. Meyer. Different tips for high-resolution atomic force microscopy and scanning tunneling microscopy of single molecules. *Applied Physics Letters*, 102:073109, 2013.
- [62] A.J. Heinrich, C.P. Lutz, J.A. Gupta, and D.M. Eigler. Molecule Cascades. Science, 298:1381, 2002.
- [63] D.M. Eigler and E.K. Schweizer. Positioning single atoms with a scanning tunnelling microscope. *Nature*, 344:524, 1990.
- [64] L. Bartels, G. Meyer, and K.H. Rieder. Controlled vertical manipulation of single CO molecules with the scanning tunneling microscope: A route to chemical contrast. *Applied Physics Letters*, 71:213, 1997.
- [65] M. Ormaza, N. Bachellier, M.N. Faraggi, B. Verlhac, P. Abufager, P. Ohresser, L. Joly, M. Romeo, F. Scheurer, M.-L. Bocquet, N. Lorente, and L. Limot. Singlemolecule enhanced spin-flip detection. arxiv, 1611.00534v1, 2016.
- [66] C. Moreno, O. Stetsovych, T.K. Shimizu, and O. Custance. Imaging Three-Dimensional Surface Objects with Submolecular Resolution by Atomic Force Microscopy. *Nano Letters*, 15:2257–2262, 2015.
- [67] K. Iwata, Sh. Yamazaki, P. Mutombo, P. Hapala, M. Ondráček, P. Jelínek, and Y. Sugimoto. Chemical structure imaging of a single molecule by atomic force microscopy at room temperature. *Nature Communications*, 6:7766, 2015.

- [68] Ch. Wagner and R. Temirov. Tunnelling junctions with additional degrees of freedom: An extended toolbox of scanning probe microscopy. *Progress in Surface Science*, 90:194–222, 2015.
- [69] F.J. Giessibl. Advances in atomic force microscopy. Rev. Mod. Phys., 75:949–983, 2003.
- [70] J. Bardeen. Tunnelling from a many-particle point of view. *Phys. Rev. Lett.*, 6:57–59, 1961.
- [71] C.J. Chen. Tunneling matrix elements in three-dimensional space: The derivative rule and the sum rule. *Phys. Rev. B*, 42:8841–8857, 1990.
- [72] C.J. Chen. Introduction to scanning tunneling microscopy, volume 2. Oxford University Press New York, 2008.
- [73] G. Mándi and K. Palotás. Chen's derivative rule revisited: Role of tip-orbital interference in stm. Phys. Rev. B, 91:165406, 2015.
- [74] J. Tersoff and D. R. Hamann. Theory of the scanning tunneling microscope. *Phys. Rev. B*, 31:805–813, 1985.
- [75] J. Cerdá, M.A. Van Hove, P. Sautet, and M. Salmeron. Efficient method for the simulation of STM images. I. Generalized Green-function formalism. *Phys. Rev.* B, 56:15885–15899, 1997.
- [76] N. Mingo, L. Jurczyszyn, F.J. Garcia-Vidal, R. Saiz-Pardo, P.L. de Andres, F. Flores, S. Y. Wu, and W. More. Theory of the scanning tunneling microscope: Xe on Ni and Al. *Phy. Rev. B*, 54:2225–2235, 1996.
- [77] J.M. Blanco, F. Flores, and R. Pérez. Stm-theory: Image potential, chemistry and surface relaxation. Prog. Surf. Sci., 81:403 – 443, 2006.
- [78] W.A. Hofer. Challenges and errors: interpreting high resolution images in scanning tunneling microscopy. Prog. Surf. Sci., 71:147 – 183, 2003.
- [79] K. Palotás, G. Mándi, and L. Szunyogh. Orbital-dependent electron tunneling within the atom superposition approach: Theory and application to w(110). *Phys. Rev. B*, 86:235415, 2012.
- [80] J.M. Blanco, C. Gonzalez, P. Jelínek, J. Ortega, F. Flores, and R. Perez. Firstprinciples simulations of stm images: from tunneling to the contact regime. *Phys. Rev. B*, 70:085405, 2004.
- [81] G. Kichin, C. Wagner, F. S. Tautz, and R. Temirov. Calibrating atomic-scale force sensors installed at the tip apex of a scanning tunneling microscope. *Phys. Rev. B*, 87:081408, 2013.
- [82] L. Gross, N. Moll, F. Mohn, A. Curioni, G. Meyer, F. Hanke, and M. Persson. High-Resolution Molecular Orbital Imaging Using a p-Wave STM Tip. *Phys. Rev. Lett.*, 107:086101, 2011.
- [83] N. Pavliček, I. Swart, J. Niedenführ, G. Meyer, and J. Repp. Symmetry dependence of vibration-assisted tunneling. *Phys. Rev. Lett.*, 110:136101, 2013.

- [84] L. Vitali, R. Ohmann, K. Kern, A. Garcia-Lekue, Th. Frederiksen, D. Sánchez-Portal, and A. Arnau. Surveying Molecular Vibrations during the Formation of Metal Molecule Nanocontacts. *Nano Letters*, 10:657–660, 2010.
- [85] L. Gross, F. Mohn, P. Liljeroth, J. Repp, F.J. Giessibl, and G. Meyer. Measuring the Charge State of an Adatom with Noncontact Atomic Force Microscopy. *Science*, 324:1428–1431, 2009.
- [86] L. Gross, B. Schuler, F. Mohn, N. Moll, N. Pavliček, W. Steurer, I. Scivetti, K. Kotsis, M. Persson, and G. Meyer. Investigating atomic contrast in atomic force microscopy and Kelvin probe force microscopy on ionic systems using functionalized tips. *Physical Review B*, 90:155455, 2014.
- [87] F. Mohn, L. Gross, N. Moll, and G. Meyer. Imaging the charge distribution within a single molecule. *Nature Nanotechnology*, 7:227–231, 2012.
- [88] B. Schuler, Sh. Liu, Y. Geng, S. Decurtins, G. Meyer, and L. Gross. Contrast Formation in Kelvin Probe Force Microscopy of Single π-Conjugated Molecules. *Nano Letters*, 14:3342–3346, 2014.
- [89] S. Kawai, A. Sadeghi, X. Feng, P. Lifen, R. Pawlak, Th. Glatzel, A. Willand, A. Orita, J. Otera, S. Goedecker, and E. Meyer. Obtaining Detailed Structural Information about Supramolecular Systems on Surfaces by Combining High-Resolution Force Microscopy with ab Initio Calculations. ACS Nano, 7:9098– 9105, 2013.
- [90] F. Albrecht, J. Repp, M. Fleischmann, M. Scheer, M. Ondracek, and P. Jelínek. Probing Charges on the Atomic Scale by Means of Atomic Force Microscopy. *Physical Review Letters*, 115:076101, 2015.
- [91] J.V. Barth. Molecular Architectonic on Metal Surfaces. Annual Review of Physical Chemistry, 58:375–407, 2007.
- [92] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M.V. Peters, and S. Hecht. Nanoarchitectures by covalent assembly of molecular building blocks. *Nature Nan*otechnology, 2:687–691, 2007.
- [93] I. Swart, L. Gross, and P. Liljeroth. Single-molecule chemistry and physics explored by low-temperature scanning probe microscopy. *Chemical Communica*tions, 47:9011, 2011.
- [94] F. Klappenberger, Y.-Q. Zhang, J. Björk, S. Klyatskaya, M. Ruben, and J.V. Barth. On-Surface Synthesis of Carbon-Based Scaffolds and Nanomaterials Using Terminal Alkynes. Accounts of Chemical Research, 48:2140–2150, 2015.
- [95] Y. He, M. Garnica, F. Bischoff, J. Ducke, M.-L. Bocquet, M. Batzill, W. Auwarter, and J.V. Barth. Fusing tetrapyrroles to graphene edges by surfaceassisted covalent coupling. *Naturel Chemistry*, 58:33–38, 2017.
- [96] Nemanja Kocić, Xunshan Liu, Songjie Chen, Silvio Decurtins, Ondřej Krejčí, Pavel Jelínek, Jascha Repp, and Shi-Xia Liu. Control of Reactivity and Regioselectivity for On-Surface Dehydrogenative Aryl–Aryl Bond Formation. *Journal* of the American Chemical Society, 138:5585–5593, 2016.

- [97] P. Ruffieux, Sh. Wang, B. Yang, C. Sánchez-Sánchez, J. Liu, Th. Dienel, L. Talirz, P. Shinde, C.A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen, and R. Fasel. On-surface synthesis of graphene nanoribbons with zigzag edge topology. *Nature*, 531:489–492, 2016.
- [98] Th. Dienel, Sh. Kawai, H. Söde, X. Feng, K. Müllen, P. Ruffieux, R. Fasel, and O. Gröning. Resolving Atomic Connectivity in Graphene Nanostructure Junctions. *Nano Letters*, 15:5185–5190, 2015.
- [99] Sh. Kawai, Sh. Saito, Sh. Osumi, Sh. Yamaguchi, A.S. Foster, P. Spijker, and E. Meyer. Atomically controlled substitutional boron-doping of graphene nanoribbons. *Nature Communications*, 6:8098, 2015.
- [100] L. Talirz, P. Ruffieux, and R. Fasel. On-Surface Synthesis of Atomically Precise Graphene Nanoribbons. Advanced Materials, 28:6222–6231, 2016.
- [101] F. Schulz, P. H. Jacobse, F. F. Canova, J. van der Lit, D.Z. Gao, A. van den Hoogenband, P. Han, R.J.M.K. Gebbink, M.-E. Moret, P. M. Joensuu, I. Swart, and P. Liljeroth. Precursor Geometry Determines the Growth Mechanism in Graphene Nanoribbons. *The Journal of Physical Chemistry C*, 121:2896–2904, 2017.
- [102] S. Barja, S. Wickenburg, Zh.-F. Liu, Y. Zhang, H. Ryu, M. M. Ugeda, Z. Hussain, Z. X. Shen, S.-K. Mo, E. Wong, M. B. Salmeron, F. Wang, M.F. Crommie, D. F. Ogletree, J.B. Neaton, and A. Weber-Bargioni. Observation of charge density wave order in 1D mirror twin boundaries of single-layer MoSe2. *Nature Physics*, 12:751–756, 2016.
- [103] Sh. Kawai, Vi. Haapasilta, B. D. Lindner, K. Tahara, P. Spijker, J.A. Buitendijk, R. Pawlak, T. Meier, Y. Tobe, A.S. Foster, and E. Meyer. Thermal control of sequential on-surface transformation of a hydrocarbon molecule on a copper surface. *Nature Communications*, 7:12711, 2016.
- [104] J. Berger, K. Kośmider, O. Stetsovych, M. Vondráček, P. Hapala, E. J. Spadafora, M. Švec, and P. Jelínek. Study of Ferrocene Dicarboxylic Acid on Substrates of Varying Chemical Activity. *Journal of Physical Chemistry C*, 120:21955–21961, 2016.
- [105] Ch. Wagner, N. Fournier, V.G. Ruiz, Ch. Li, K. Mullen, M. Rohlfing, A. Tkatchenko, R. Temirov, and F.S. Tautz. Non-additivity of molecule-surface van der Waals potentials from force measurements. *Nature Communications*, 5:5568, 2014.
- [106] H. Hölscher, S. M. Langkat, A. Schwarz, and R. Wiesendanger. Measurement of three-dimensional force fields with atomic resolution using dynamic force spectroscopy. *Applied Physics Letters*, 81:4428–4430, 2002.
- [107] M. Ternes, Ch. P. Lutz, C.F. Hirjibehedin, F.J. Giessibl, and A. J. Heinrich. The Force Needed to Move an Atom on a Surface. *Science*, 319:1066–1069, 2008.
- [108] B.J. Albers, T.C. Schwendemann, M.Z. Baykara, N. Pilet, M. Liebmann, E. I. Altman, and U. D. Schwarz. Three-dimensional imaging of short-range chemical forces with picometre resolution. *Nature Nanotechnology*, 4:307–310, 2009.

- [109] A. Sweetman, M.A. Rashid, S.P. Jarvis, J.L. Dunn, Ph. Rahe, and Ph. Moriarty. Visualizing the orientational dependence of an intermolecular potential. *Nature Communications*, 7:10621, 2016.
- [110] S. Grimme. Accurate description of van der Waals complexes by density functional theory including empirical corrections. *Journal of Computational Chemistry*, 25:1463–1473, 2004.
- [111] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.*, 92:246401, 2004.
- [112] J. Klimeš, D. R. Bowler, and Michaelides A. Chemical accuracy for the van der Waals density functional. J. Phys.: Cond. Matt., 22:022201, 2010.
- [113] A. Tkatchenko and M. Scheffler. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.*, 102:073005, 2009.
- [114] E. Arunan, G.R. Desiraju, R.A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R.H. Crabtree, J.J. Dannenberg, P. Hobza, H.G. Kjaergaard, A.C. Legon, B. Mennucci, and D.J. Nesbitt. Defining the hydrogen bond: An account (IUPAC Technical Report). *Pure and Applied Chemistry*, 83, 2011.