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# MOBILITY OF COMPLEX ORGANIC SPECIES AT METAL SURFACES

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**Abstract**. Concepts, recent developments and achievements in investigations addressing the mobility of complex organic molecules on welldefined metal surfaces are reviewed.

*Keywords*: Adsorption; surface diffusion; molecular rotors; self-assembly; metal surfaces; Scanning Tunneling Microscopy; molecular nanoscience.

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# 0. Introduction

The motion of complex organic molecules plays a decisive role in the positioning of functional molecular species at selected sites of templates and the self-assembly of supramolecular nanostructures or layers at surfaces. Both translational and rotational motions need to be considered, and moreover,

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conformational changes may interfere. The detailed understanding of such phenomena is a mandatory issue in the present race for nanoscale control of matter and the development of future nanostructured functional materials, nanofabrication methodologies and devices. But also from the fundamental research point of view this field is rewarding, because it comprises new horizons and challenges in the exploration of the molecular world.

The first ideas about molecular mobility at surfaces date back to the 1920's [1–3]. Notably, detailed light microscopy observations in the crystallization of benzophenone provided indirect evidence that 'molecules can migrate on the surface by virtue of thermal motion' [3]. Based on these and other observations, Volmer suggested 'the following conception of the mechanism of the spreading over solid surfaces: at low enough temperatures the adsorbed molecules ... are mostly bound to the fixed atoms of the underlying material, and like these only oscillate around their equilibrium positions. When, with rising temperature, the amplitude of the oscillations is increased, it will occur more and more often that an adsorbed molecule, because of an occasional elongation, jumps into the unoccupied field of an adjacent atom. The process therefore requires a definite energy of activation and its velocity will increase as the temperature rises in accordance with an exponential law' [3]. This interpretation is in agreement with the thermionic observations from Becker and Taylor, which were at the origin to associate surface diffusion with 'hopping atoms' [4,5]. These basic conceptual views are valid to date. However, in the last decades, tremendous progress has been made in both the experimental characterization and theoretical understanding of surface mobility, and the foundations and advances of this field have been extensively reviewed [6–21].

With the advent of modern surface and nanoscience experimental tools, comprehensive investigations of the motion of complex molecular adsorbates at atomically clean surfaces under ultra-high vacuum conditions (UHV) became possible. In initial studies integral techniques such as laser-induced thermal desorption (LITD) were employed to create concentration gradients in organic layers at well-defined metal substrates and measure their temporal decay [22]. The invention of the scanning tunneling microscope (STM) [23], which revolutionized surface science and was key in the development of nanoscale science, introduced the possibility to perform observations at the single molecule level.

# 1. Basics and Methodology

Molecules coming from the gas phase into contact with a metal surface thermalize with the phonon heat bath of the crystal upon adsorption. The



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Fig. 1. STM images resolving (a) the hexagonal atomic structure of the close-packed fcc(111) surface and (b) the anisotropic fcc(110) surface of Ag. The surface unit cells and high symmetry directions are marked. (c) Schematic one-dimensional potential energy surface experienced by a simple individual adsorbate along a high-symmetry surface direction ( $E_m$ : migration energy barrier;  $E_b$ : bonding energy; *a*: surface lattice constant).

admolecule similarly experiences the periodic corrugation of the substrate atomic lattice, which is illustrated in Fig. 1. The binding energy is thus subject to lateral variations with local minima corresponding to energetically favorable positions. These adsorption sites are separated by energy barriers being usually significantly smaller than the energy barrier for desorption. For isolated adspecies the minimum energy difference between adjacent sites is called the migration energy barrier  $E_m$ . In the case of anisotropic surfaces direction dependent migration barriers along principal crystal axes can be present [20].

The excitation and damping of the thermal motion of an adsorbate is predominantly mediated by the coupling to the substrate phonon bath. The typical frequency of the phonons is  $\sim 10^{12}-10^{13} \text{ s}^{-1}$ , with surface atom vibrational amplitudes of  $\sim 0.1$  Å at room temperature. The magnitude of the thermal energies with respect to the migration energy barrier is decisive for the lateral transport of adsorbates on the surface. In most practical situations the condition  $k_BT \ll E_m$  is obeyed. When the thermal energies are very small, the adsorbates are confined to specific sites, corresponding generally to high-symmetry positions on the surface. A temperature can be

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identified where the adspecies can be considered immobile with respect to a time scale of interest (quantum mechanical tunneling transport is not considered here, cf. Refs. [13,19,20]). For temperatures exceeding this value, surface migration is driven by the continuous energy exchange between adsorbate and substrate. The corresponding energy fluctuations result in random jumps from one energy minimum to another, i.e., a stochastic hopping mechanism is operative. Most of the time the adsorbates remain in the adsorption well, where they are vibrating, and only rarely the energy necessary to overcome the migration barrier is accumulated. Hence it is frequently assumed that subsequent jumps are uncorrelated, i.e., that hopping is a Markov process. Upon averaging over many events, a hopping rate can be defined.

On the one hand the aleatoric thermal mobility of adsorbed particles is called surface diffusion. This 2-D brownian motion is a stochastic process reflecting the never ceasing energy fluctuations of a system in thermal equilibrium in the absence of external forces at finite temperature. When the particles are adsorbed on a homogenous surface and do not interact with each other, this leads to random walks. On the other hand, a directed flux of adsorbates can be induced by the variation of their density or chemical potential at the surface. This corresponds to a gradient-driven transport phenomenon for a system which is not in thermodynamic equilibrium. In its simplest form it can be described by Fick's law, where the concentration gradient is the driving force. With increasing time, the resulting 2-D directional diffusion smears out an initial concentration profile. When eventually equilibrium is attained, there is a uniform adsorbate distribution on the surface and no further net surface mass transport takes place; nevertheless the aleatoric thermal mobility persists. In both cases there is a strong temperature dependence. The higher the temperature, the more active the adsorbate motion and the faster the gradient decay.

# 1.1. Tracer diffusion and the hopping model

In the hopping model, the migration of an isolated adspecies corresponds to an aleatoric walk from adsorption site to adsorption site for a system in thermodynamic equilibrium. Upon denoting the starting point of the motion at t = 0 as  $r_o + (x_o, y_o)$ , the mean jump length along the x, ydirections as  $\langle \lambda_x \rangle$ ,  $\langle \lambda_y \rangle$  and the corresponding hopping frequencies as  $\Gamma_x$ ,  $\Gamma_y$ , the mean square displacement of the atom is:

$$\langle (r(t) - r_o)^2 \rangle \equiv \langle (\Delta r)^2 \rangle = (\Gamma_x \langle \lambda_x \rangle^2 + \Gamma_y \langle \lambda_y \rangle^2) t$$

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which reduces for an isotropic surface to:

$$\langle (\Delta r)^2 \rangle = \Gamma_h \langle \lambda \rangle^2 t.$$

A characteristic property of surface migration is that  $\langle (\Delta r)^2 \rangle$  varies linearly with time. Note that the very definition of a hopping frequency  $\Gamma_h$  tacitly implies statistic averaging over many hopping events. The time difference between the individual jumps of a specific particle varies stochastically. The corresponding *tracer diffusion coefficient* is defined as:

$$D^* = \lim_{t \to \infty} \frac{\langle (\Delta r)^2 \rangle}{2dt}$$

where d is the dimensionality of the diffusion process (d = 1, 2 at surfaces). Combining the above equations it follows that  $D^*$  can be expressed in terms of the hopping rate  $\Gamma_h$  and the mean jump length  $\langle \lambda \rangle$ :

$$D^* = \frac{1}{2d} \langle \lambda \rangle^2 \Gamma_h.$$

When  $k_B T \ll E_m$ , the tracer diffusion coefficient obeys an Arrhenius law and accordingly the following relation holds:

$$D^* = \frac{1}{2d} \langle \lambda \rangle^2 \nu_o \exp[-\beta E_m] \equiv D_o^* \exp[-\beta E_m]$$

where  $\nu_o$  is designated as the *attempt frequency*,  $D_o^*$  as the *pre-exponential factor* (or *prefactor*) of the tracer diffusion,  $\beta = [k_B T]^{-1}$ . A unique migration barrier is posed. This equation is fundamental in surface migration. When nearest-neighbor jumps prevail,  $\langle \lambda \rangle$  is equal to the surface lattice constant *a*. Since  $a \sim 3$  Å and since the attempt frequency can be associated with the vibrational frequency of the atom in the adsorption well (typically  $10^{13} \text{ s}^{-1}$  [24]), the pre-exponential factor is expected to be  $\sim 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ , which is frequently considered as a universal value.

# 1.2. Concentration gradients and mass transport

Gradient-driven diffusion phenomena at finite coverages are usually described in macroscopic terms via an adsorbate flux density in two dimensions. The *chemical* or *collective diffusion* coefficient  $\tilde{D}$  is accordingly defined through Fick's laws. The first of these empirical laws describes the diffusion flux density **j** across a borderline, which results from a coverage

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gradient in a continuum:

$$\mathbf{j} = -\tilde{D}(\Theta)\nabla_r\Theta(r,t)$$

upon combination with the continuity equation  $-\partial_t \Theta(r,t) = \nabla_r \mathbf{j}$ , Fick's second law is obtained:

$$\partial_t \Theta(r,t) = \nabla_r \cdot D(\Theta) \nabla_r \Theta(r,t)$$

The collective diffusion coefficient is thus relevant for the mass-transport at surfaces in systems, which are not in thermodynamic equilibrium. It generally depends on coverage. The above diffusion equation is widely employed to determine  $\tilde{D}$ , since the adsorbate concentration is a measurable quantity. In practice, frequently the decay of an adjusted coverage gradient is analyzed and diffusion equation is solved numerically or analytically for a given geometry. This task is considerably simplified when diffusion coefficients independent of coverage exist or may be assumed and:

$$\partial_t \Theta(r,t) = D \nabla_r^2 \Theta(r,t).$$

Collective diffusion on homogenous substrates usually obeys an Arrhenius law under conditions where it can be conveniently measured. Accordingly, the data are analyzed assuming that energetics and dynamics can be factorized, i.e.:

$$\tilde{D}(\Theta) = \tilde{D}_o \exp[-\beta E_d].$$

The barrier for chemical or collective diffusion  $E_d$  is then obtained using the relation:

$$E_d = -\partial_\beta \ln \tilde{D}$$

It is important to note that the migration barrier  $E_m$  of isolated adsorbates and the barrier encountered in collective diffusion  $E_d$  are *a priori* unequal, although they are related and become identical in the zero coverage limit [13,20].

# 1.3. Rotation of adsorbed molecules

For the case of adsorbed complex molecules, which generally have a preferred orientation with respect to the substrate atomic lattice in their energy minimum configuration, the possibility of 2-D molecular rotations needs to be considered. These rotations require thermal activation, analogous to lateral transport. In the simplest case they imply the overcoming of a unique rotation energy barrier  $E_r$ , which may be higher, equal or lower than the

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diffusion or migration barrier.  $E_r$  is associated with a corresponding rotational prefactor.

As an exemplaric study with a simple molecular adsorbate, we refer to a recent STM study of  $C_2H_2$  on Cu(001) where both molecular rotation and diffusion could be monitored [25]. Each process was found to obey an Arrhenius law. The activation energy for diffusion (rotation) is  $530 \pm$ 10 meV ( $169 \pm 3 \text{ meV}$ ) with a prefactor of  $10^{13.6\pm0.2} \text{ s}^{-1}$  ( $10^{11.8\pm0.2} \text{ s}^{-1}$ ). At lower temperatures, rotations induced by the tunneling current could be monitored (cf. Fig. 2(a)). It was proposed that they are mediated by the coupling of vibrational excitations to the rotational motion [26,27]. An STM study with the complex species hexa-*tert*-butyldecacyclene (HBDC) on Cu(100) provided evidence for continuous rotation of a single molecule at room temperature laterally confined in a vacancy of an organic layer, as schematically illustrated in Fig. 2(b) [28,29].



Fig. 2. (a) Frustrated rotational motion of  $C_2H_2$  adsorbed on a Cu(001) surface induced by tunneling electrons at 8 K. The model shows top and side views of the molecular adsorption site with the C-C bond parallel to the surface and the preferred angular orientations. In the corresponding STM data the configurations of a specific  $C_2H_2$  molecule at the same adsorption site with respect to the Cu substrate (indicated as a square lattice) are illustrated [26]. (b) Model illustrating the rotation of the complex molecule hexa-*tert*-butyldecacyclene on a square substrate [29].

# 1.4. Laser-induced thermal desorption

In the 1980's a versatile technique based on laser-induced thermal desorption (LITD) was introduced for the investigation of surface diffusion phenomena [30]. LITD is conceptionally straightforward. A specific homogeneous concentration of adsorbates is established on a surface.

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Subsequently a well-defined area at the surface is depleted from the adsorbate layer by a focused laser pulse. Since thermal equilibrium at the surface is rapidly recovered, the bare spot can be refilled only by surface diffusion of adsorbates from the surrounding areas [31]. A second laser impulse is applied to desorb the transported adsorbates after a time interval t from the first pulse. The corresponding amount of material can be quantified by mass spectrometry. For the idealized case of a circular depletion region, with a step-like coverage gradient and a concentration-independent diffusivity, the time-dependent refilling from Fick's first law is [32,33]:

$$\frac{S(t)}{S(\infty)} = 1 - 2 \int_o^\infty \frac{J_1^2(\frac{r}{r_o})}{\frac{r}{r_o}} \exp\left(-\frac{\tilde{D}t}{r_o^2}\left(\frac{r}{r_o}\right)^2\right) d\left(\frac{r}{r_o}\right)$$

where S(t) is the measured signal,  $r_o$  is the radius of the depleted area and  $J_1$  is a Bessel function of order 1.  $r_o$  is typically in the 100  $\mu$ m range. Upon measuring the fractional refilling for several time intervals at a given temperature, the diffusivity can be determined from fits using the above equation or analogous expressions for other geometries to the experimental data.

Experiments performed with different initial coverages provide trends for the coverage dependence of the diffusivity. LITD has been employed for investigating surface mobility of adsorbed gases and large molecules on single crystal surfaces. Among this technique's advantages are the possibility to study virtually all adsorbates and coadsorbate systems which can be thermally desorbed and detected by mass spectrometry. A frequently discussed problem is the possible effect of substrate imperfections in the area under investigation, which may be even created upon irradiation [34]. Diffusion over atomic steps is of course inevitable for the mesoscopic mass transport in the experiments. Coverage-independent diffusivities are frequently assumed for the data interpretation, and it was pointed out that the concentration variation in the depletion area affects the corresponding results [35–37].

# 1.5. Scanning tunneling microscopy

STM measurements can be employed to systematically study tracer diffusion by following adsorbate migration at the atomic level *in situ*. This was achieved for a variety of systems, including adsorbed gas atoms and molecules at metal surfaces [20]. Moreover, STM allows for detailed investigation of the bonding geometries and 2-D rotational motions. The temperature dependence is conveniently investigated by variable-temperature

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instrumentation [38–42]. In most cases, hopping frequencies were determined from a statistical analysis of series of STM images, whence the corresponding activation energies and prefactors can be extracted from Arrhenius plots. With favorable systems the mean square displacement of adatoms can be determined and the jump mechanims elucidated [43,44]. The recently presented 'atom tracking' method allows to follow the migration path of an individual moving adsorbate [45]. With very sophisticated instruments, surface mobility can be even recorded at video rates and visualized by STM movies [43,46]. The complete analysis and interpretation of such data can only be achieved with the development of adequate computer techniques [43,47]. Care must be taken to exclude the possible effect of tipsurface interactions in STM experiments. Both theoretical and experimental studies indicate a modified migration energy barriers under the STM tip [48–53]. However, such effects are negligible or can be largely excluded by working at large tunneling electrode distances. Among the limitations of STM studies are also the rather low diffusivity ranges accessible and its principal application to small adsorbate concentrations.

The striking advantages of STM are atomic resolution, its conceptional transparency and versatility, and the appeal of direct visualisation. STM can be applied to study anisotropic surface mobility, diffusion on inhomogeneous surfaces, or adsorbate interactions and collective transport effects on a local scale. It also a technique where a simultaneous characterization of tracer and chemical diffusion on single crystals is feasible [54]. Surface mobility studies using STM are currently progressing rapidly.

# 2. Case Studies Addressing Mobility of Complex Molecules at Metal Surfaces

A fair number of studies on the surface mobility of adsorbed complex molecules can be found in the literature. Techniques applied so far are LITD and STM. The investigated adsorbates cover the range from small molecules with simple adsorption configurations to large organic molecules which exceed by far the dimensions of the respective substrate unit cells. In any case additional degrees of freedom need to be considered. These include rotational motions or the occupation of multiple adsorption sites. With large and flexible species moreover conformational changes may be of importance in adsorption [55–58] and hence interfere in the surface transport properties [59]. Exemplaric investigations are discussed in the following.

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Systematic observations on the mobility of *n*-alkanes (propane, *n*-butane, *n*-pentane and *n*-hexane with the chemical formula  $C_nH_{2n+2}$ ) on Ru(001) were performed with LITD [22]. Arrhenius behavior is obeyed in all cases and it was found that the diffusion barrier increases linearly with the alkane chain length from  $130 \pm 10$  to  $210 \pm 10$  meV, whereas only small variations in the prefactors (~0.15 cm<sup>2</sup> s<sup>-1</sup>) exist [22] (cf. Fig. 3). The observed diffusion coefficients are quite independent of coverage, indicating small lateral interactions. It was suggested that the *n*-alkanes move in a rigid configuration on the surface [22]. Related investigations employing pentane isomers revealed diffusion barriers scaling inversely with the degree of branching of the isomers [60]. Upon fluorination of *n*-butane both the diffusion barrier and the prefactor were found to be lowered [61]. Recent Helium atom scattering (HAS) observations with octane on Ru(001) indicate that electron-hole pair creation is involved in the damping of the molecular motion [62].

The observations of the *n*-alkane diffusion triggered extensive theoretical investigations, mostly employing Monte Carlo (MC) and Molecular Dynamics (MD) simulations [63–69]. From systematic simulations of a series of *n*-alkanes  $(n-C_3H_8, n-C_6H_{14}, n-C_{10}H_{22} \text{ and } n-C_{20}H_{42})$  on W(001) the trends observed experimentally on Ru(001) were confirmed in the 300–1000 K



Fig. 3. Arrhenius plots of the surface diffusion coefficients for a series of *n*-alkanes adsorbed on Ru(001) at  $\theta = 0.2\theta_{sat}$ . LITD results [22].

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range (i.e., Arrhenius behavior, increase of  $E_m$  with the chain length), albeit with significantly smaller prefactors close to  $1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  [63].

In a recent detailed transition state theory (TST) study of *n*-alkane (n-butane — n-decane) diffusion on Pt(111) the respective diffusion mechanisms were addressed in detail. It was found in particular that the hopping between nearest neighbor sites is not strictly obeyed and directional anisotropy can be induced by the molecular orientation [66]. In addition, the motion of larger molecules involves transient occupation of local minima. Some typical diffusion paths are illustrated in the model shown in Fig. 4. Again, the theoretical prefactors were found to be close to the universal value. In related theoretical studies the diffusion and spreading of chain-like molecules on solid surfaces was considered [70,71]. Chains were modeled as connected segments occupying sites on a square lattice, whereby the chain flexibility and attractive interactions can be varied [70]. The coverage and interaction dependence of tracer and collective diffusion coefficient calculated from MC simulations have been obtained. Further aspects are considered in Refs. [72–74].

A systematic STM study was reported for the thermal migration of the complex molecule PVBA (4-trans-2-(pyrid-4-yl-vinyl) benzoic acid) on Pd(110) [75]. This rigid and large organic molecule interacts strongly with the Pd substrate and binds diagonally to two neighboring Pd troughs (cf. Fig. 5). No changes in the adsorption geometry exist at different coverages [76]. The diffusion of single molecules is strictly 1-dim in  $[1\bar{1}0]$ , i.e., along the Pd surface atom rows, whereby the molecular orientation is strictly



Fig. 4. Selected molecular configurations involved in (a) *n*-hexane and (b) *n*-butane and *n*-octane hopping on Pt(111) along easy migration paths. The molecular motion follows the sequence 1-2-3 in (b). Filled (open) circles indicate the carbon backbone position of the molecule at the binding site (transition state), diamonds correspond to Pt surface atoms [66].

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Fig. 5. Surface diffusion of the rigid rodlike molecule 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid on Pd(110). In (a) and (b) two consecutive STM images taken at 361 K are shown which demonstrate the 1-dim motion. Arrows indicate molecules whose position changed; circles mark fractionally imaged molecules moving under the STM tip in the course of the measurement. (c) Model for the flat adsorption geometry explaining the two observed molecular orientations in the STM data. The length of the molecule is 12.5 Å. (d) Arrhenius plot of single molecule hopping rates [75].

retained, as demonstrated by the data reproduced in Fig. 5. It obeys an Arrhenius law with a diffusion barrier of  $830 \pm 30 \text{ meV}$  and a prefactor of  $7.6 \times 10^{-6\pm0.4} \text{ cm}^2 \text{ s}^{-1}$  [75]. In subsequent related investigations the motion of individual buckyballs adsorbed on Pd(110) system was investigated. The migration barrier for 1-D motions along the substrate furrows of adsorbed C<sub>60</sub> monomers was determined to  $1.4 \pm 0.2 \text{ eV}$  with a prefactor of  $10^{14.4\pm0.4} \text{ s}^{-1}$  [77]. It was not possible to determine possible buckyball orientational changes during the motion, which effectively might 'roll' over the surface.

An intricate diffusion limited scenario was observed in the lowtemperature aggregation of PVBA and the related species PEBA (4-[(pyrid-4-yl-ethynyl)]-benzoic acid) on Ag(111) [78,79]. The operation of anisotropic hydrogen bonding between the molecular endgroups in conjunction with the smoothness of the substrate leads to the formation of molecular networks, as demonstrated by the STM data in Fig. 6. At higher

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Fig. 6. (a) Diffusion limited aggregation of 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid lying flat on Ag(111). The hydrogen bonding between the molecular endgroups stabilizes a molecular network upon adsorption at T = 125 K. (b) For the H-bond mediated selfassembly of molecular twin chains in equilibrium (~250–400 K) both rotational and translational molecular mobility is required [78,79].

temperatures, the PVBA molecules self-assemble at the surface to extended molecular twin chain gratings (2-D islands), which are again stabilized by hydrogen bonding. The formation of such superstructures provides indirect evidence of both rotational and translational molecular rearrangements [78,79], which are similarly operative in the self-assembly of other hydrogenbonded supramolecular nanostructures other substrates [80–85].

A detailed comparative STM study on the motion of the related molecules HBDC and decacyclene (DC) on the Cu(110) surface revealed that with this system long jumps, i.e., hopping events spanning multiple lattice spacings are dominating the 1-D tracer diffusion of these species [86] (a STM movie can be found at http://www.phys.au.dk/ camp/stmmovies.shtm). The chemical structure, exemplaric STM observations and Arrhenius plots for hopping rates are shown in Fig. 7. Both molecules comprise an aromatic  $\pi$  system and adsorb in a flat geometry on the substrate, whereby the presence of the additional tert-butyl aromatic side groups in HBDC is expected to raise the aromatic system away from the surface. This geometrical difference goes along with marked differences in the migration barriers, prefactors and mean jump lengths  $\langle \lambda \rangle$ for DC (HBDC) molecular displacements along the  $[1\overline{1}0]$  direction, which were determined to  $0.74 \pm 0.03 \ (0.57 \pm 0.02) \, \text{eV}, \ 10^{13.9 \pm 0.7} (10^{13.5 \pm 0.4}) \, \text{s}^{-1}$ and  $3.9 \pm 0.2$  (6.8  $\pm 0.3$ ) substrate spacings, respectively. The intriguing possibility exists that the diffusion of such species could be coupled to a disk-like rotation [58]

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Fig. 7. (a), (b) The complex molecules decacyclene (DC) and hexa-tert-butyldecacyclene (HBDC). (c) Stills from an STM movie of HBDC migration on Cu(110) arrows indicate displacement directions for molecules in the subsequent image  $(T = 194 \text{ K}; 50 \times 50 \text{ nm}^2; \Delta t = 13.9 \text{ s}).$  (d) Arrhenius plots of the hopping rates and tracer diffusion constants for both molecules [86].

Finally we address an STM study providing direct insight into the formation of coordination compounds at a Cu(100) surface, whereby translational and rotational molecular motions are involved. Towards this goal a molecular building block — 1,3,5-benzenetricarboxylic acid (trimesic acid, tma) — was deposited on the copper substrate. At room temperature the carboxylic acid moïeties deprotonute and the resulting trimesate admolecules

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Fig. 8. tma-molecules bond in a flat adsorption geometry at a copper surface and are resolved as equilateral triangle in STM. The sequence of STM images reveals how the thermal motion of molecules at the surface proceed: following tma rotational motions and displacements a Cu atom is captured whereupon a cloverleaf-shaped Cu(tma)<sub>4</sub> coordination compound evolves (second image for t = 80 s, central Cu atom highlighted in red) [87].

bind flat on the surface, where they coexist with a 2-D gas of highly mobile Cu adatoms, originating from the continuous atom evaporation at atomic steps. These Cu adatoms can bind to the reactive ligands of the molecule, i.e., the carboxylate groups. In STM image sequences, such as the one reproduced in Fig. 8, the movements of single molecules were monitored revealing how rotating tma molecules act as dynamical atom trap for individual Cu atoms (for a respective movie: http://www.mpi-stuttgart.mpg.de/kern/Res\_act/supmat\_2.html). Thus single events of association and dissociation of cloverleaf-shaped Cu(tma)<sub>4</sub> coordination compounds were directly observed. Furthermore it turned out that the lifetime of the complexes depends crucially on the local chemical environment [87].

# 3. Future Perspectives

The comprehensive investigation and understanding of the mobility of complex adsorbed molecules is a challenging and fruitful ground for experimental and theoretical investigations. The examples presented on the previous pages reveal that the pertaining research is currently at an early stage. Much remains to be learned about the detailed nature of the mechanisms underlying the motion of complex adsorbed species, notably when they include conformational adaptation, rotations or substrate rearrangements. The most promising experimental technique in this respect is at the present stage temperature controlled STM, especially when instrumentation with high data acquisition rates is employed. With systematic investigations a general phenomenological description of the molecular motion may emerge. Furthermore, in view of the recent progress in computational science, the

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interplay between experiment and modeling is expected to heavily contribute to a comprehensive understanding and may even culminate in the development of a rationale to predict properties or at least trends for any system of interest.

It is thus believed that studies advancing this field will be a continuous source of further scientific insight and inspiration. Moreover, the current trends in nanoscale science and technology suggest that supramolecular assemblies built up from appropriate molecular building blocks will play an important role in the future development of highly organized functional materials and nanosystems. When suitable processes are conducted using appropriate building blocks at surfaces or prestructured templates, entirely novel low-dimensional architectures can be realized. In this case the motions and interactions of the adsorbed complex species are decisive elements to rationalize and steer the respective self-assembly protocols. Hence we expect that the basic understanding elaborated today will be useful for the design of tomorrow's materials and devices.

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