DOI: 10.1002/anie.200704110

Spectroscopic Characterization and Deliberate Modification of a Single Molecule by Tunneling of Electrons

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adsorption · heterogeneous catalysis · scanning probe microscopy · surface chemistry · vibrational spectroscopy

The modification of molecules by reactions with atoms or other molecular species is a synonym for chemistry. Whereas many properties, for example, color, odor, or hardness, of the products obtained by a chemical reaction can be determined without any tools, the unraveling of the atomistic structure of a molecule requires advanced techniques, some of them rather sophisticated. Historically, diffraction methods were the first to provide the details of the structure of a molecule. Today, with advanced hardware and software tools, atomic coordinates can be determined by X-ray diffraction (XRD) even for large molecules—if macroscopic crystallites of high quality are available. Later, spectroscopic techniques were introduced which allow a structure determination for a few molecules or even a single molecule without the necessity of crystalline order as required by XRD. These techniques, like NMR or IR spectroscopy, are, however, indirect, and reference samples or extensive simulations are needed.

When the scanning tunneling microscope (STM) was introduced, it became obvious very soon that this technique is capable of directly imaging molecules deposited on a suitable support. Although, of course, it had been known since Kekulé that benzene is a ring molecule, the first STM image of a benzene molecule deposited on a Rh surface, reported in 1988,[1] made it to the covers of many journals.

That a direct chemical identification of molecular species on a surface from the STM topographs alone is a difficult task, however, became apparent from work carried out in the following years. First it was shown by theoretical work[2] that the threefold (and not sixfold) symmetry visible in the benzene STM micrographs was not caused by a Kekulé-type distortion (i.e. the C–C bonds in the benzene ring becoming inequivalent as a consequence of the interaction with the Rh substrate) but were caused by electronic effects originating from the metal substrate. Subsequent STM work directly demonstrated that the apparent shape of a benzene molecule in STM images in fact varies quite strongly when placed on different sites on a metal surface.[3] A number of other examples showed later that the many hopes triggered by the introduction of the STM with regard to single-molecule chemistry could not be fulfilled because of a lack of chemical sensitivity.

This situation was rather disappointing, since shortly after demonstrating that the STM technique can be applied to molecules in a rather straightforward fashion, Eigler and coworkers in a pioneering work used the tip of an STM not only to image but also to manipulate particles adsorbed on a metal substrate.[4] This first demonstration was for noble-gas atoms, but shortly after also individual CO "ligands" on a Pt surface could be positioned using the STM tip.[5] Furthermore, very soon it was realized that molecules could not only be moved but could also be chemically modified.[6] Whereas this first demonstration was a dissociation, later also the synthesis of a single biphenyl molecule could be obtained by first dissociating two iodobenzene adsorbates and then connecting the two phenyl rings.[7] Very recently, also the tip-induced tautomerization of naphthalocyanine adsorbed on a NaCl surface has been reported.[8] In all these cases, however, an unambiguous chemical identification of the reaction products and the intermediates was not possible.

Imaging a single reactant molecule, adding atoms or molecular species in a step-by-step fashion just like building a molecule from a ball-and-stick model set, unambiguously characterizing the intermediates and the reactant, and then reversing the reaction, however, still remained a dream.

Possibly the most important step to make this chemist's dream finally come true was the demonstration that the STM tip can be used as a spectrometer with high local specificity to determine the vibrations of molecular adspecies bound to a substrate,[9] thus providing the required chemical sensitivity. This technique, also referred to as IETS (inelastic electron tunneling spectroscopy), is based on recording the tunneling current as a function of the applied voltage and is related to an older technique known under the same name, which had been introduced to study molecular vibrations at metal/oxide/metal junctions.[10] The realization of the dream, initiating reactions for molecules on a "tablet" in a controlled fashion, seemed to come within reach.

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Recently, in a paper by Katano et al.,[11] this task has been accomplished and a cyclic reaction involving the de- and subsequent rehydrogenation of a molecular species on a metal surface has been studied and characterized in detail. These experiments were carried out for a nitrogen-containing organic molecule, methylaminocarbyne ($CNHCH_3$), adsorbed on a platinum surface at cryogenic temperatures.[12] First, the molecule was imaged with an STM. The proof that the protrusions seen by the STM (Figure 1) really correspond to intact molecules—and not to a minority species or molecular fragments resulting from a tip-induced dissociation—is difficult to achieve on the basis of the STM topographs alone. In these experiments the authors used the above-mentioned STM method to record a vibrational spectrum of the molecule below the STM tip to obtain an unambiguous chemical identification of the molecular species. The Pt–CNHMe stretching vibration at 34 meV clearly demonstrates the presence of an intact methylaminocarbyne.

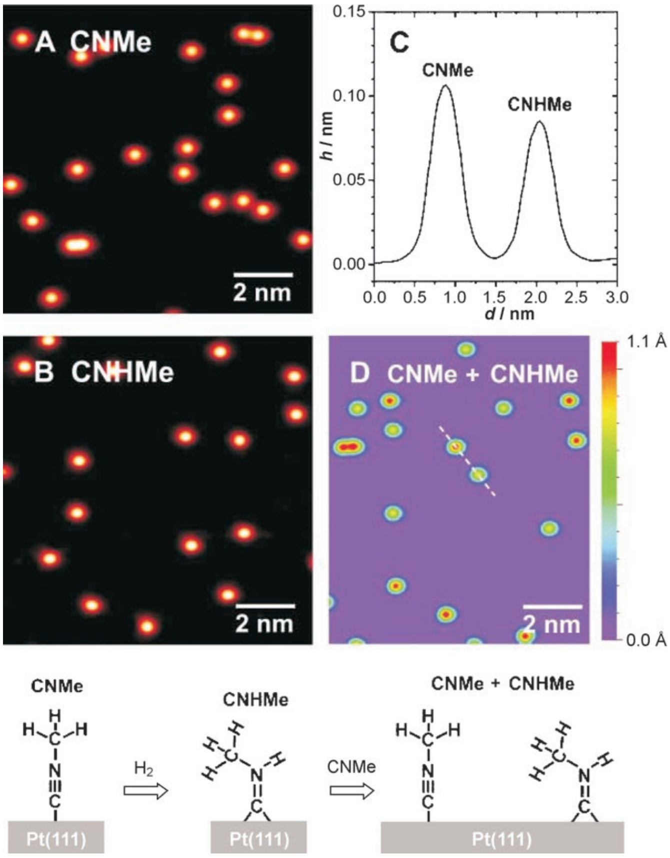

Figure 1. A) STM image of CNMe adsorbed on Pt(111). B) STM image of CNHMe on Pt(111) obtained after exposure of the CNMe/Pt(111) surface to H_2 at 300 K. CNMe and CNHMe are resolved as protrusions, and the difference in the apparent heights (h) as shown in (C) (h(CNMe) = 0.106 nm and h(CNHMe) = 0.085 nm) is confirmed by an image obtained when CNMe was added to the CNHMe/Pt(111) surface (D). The line profile shown in (C) is taken from the dashed line indicated in (D). A schematic representation of the molecular species present in (A), (B), and (D) is shown at the bottom. Reproduced with permission from reference [11].

Then, in the next step Katano et al. used the tip of the STM to selectively break the N–H bond in the weakly adsorbed aminocarbyne to yield the methylisocyanide. This H cleavage was accomplished by a voltage pulse (3.0 V, 1.5 nA for 1 s), yielding electrons tunneling from the tip into the adsorbate and thus transferring energy to the molecule. The STM images of the isocyanide adsorbate were very similar to those observed for the reactant; the only difference was that the protrusions seen in the STM data are 0.2 Å higher for the cyanide than for the aminocarbyne. The proof that this higher protrusion corresponds to an adsorbed isocyanide species had again to be carried out by STM-based vibrational spectroscopy. The reaction product was identified unambiguously by observation of the Pt–CNMe vibration at 48 meV, which has also been observed by another vibrational spectroscopy, EELS (electron energy loss spectroscopy).[13]

Finally, by adding hydrogen molecules to the gas phase above the Pt substrate, hydrogen molecules adsorbed on the metal surface, dissociated, and yielded a small coverage of H-adatoms. In the last step of the cyclic reaction—the only step not directly triggered by the STM tip—the H atoms reacted with the methylisocyanide molecule to again form the original aminocarbyne (identified by IETS), thus yielding a full cycle by restoring the product back to the reactant. Thus, a complete reaction cycle of dehydrogenation and subsequent hydrogenation could be performed for a single molecule.

These experiments demonstrate that controlling reactions of single molecules and the identification of reactants, products, and intermediates using an STM carry an enormous potential for understanding chemical processes. After the applicability and the potential of the method have now been demonstrated for well-known reactions, in a next step this approach will be used to study fundamental principles of chemical reactions catalyzed at metal surfaces. One can foresee that with this approach the different reactivities of surface structures (flat areas, step edges, kink sites, vacancies, and foreign adatoms) can be investigated in detail; in particular, it will be possible to identify active sites for catalytic processes at solid supports. To give an example, after exposure of a substrate to a particular molecule, STM together with IETS can be used to identify whether adsorption-induced chemical modifications of an adsorbate depend on the nature of the adsorption site, for example, whether dehydrogenation reactions often accompanying the adsorption of H-containing molecules on transition-metal surfaces are more likely to occur at step edges or at kink sites.

A remaining major challenge in this field is the fact that, in contrast to bulk IR spectroscopy and EELS, the selection rules that define which vibrations of an adsorbed molecule can be seen in the STM–IETS data are still missing. Considering the substantial theoretical effort in this area, however, it can be expected that this knowledge will become available in the next few years and will allow chemists to make an STM-based analysis of reaction paths a more generally applicable tool in surface chemistry and will in particular open a new approach to understanding principle phenomena in heterogeneous catalysis.

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