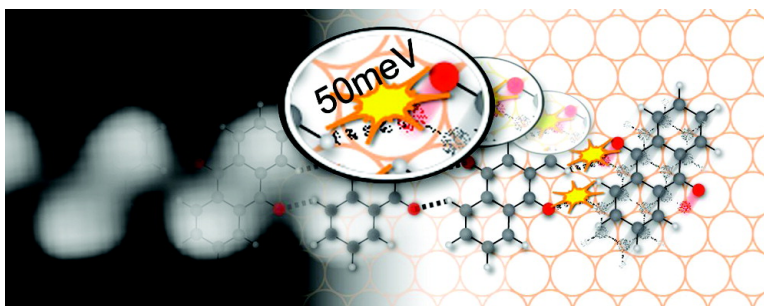Communication

A Quantitative Approach to Hydrogen Bonding at a Metal Surface

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A Quantitative Approach to Hydrogen Bonding at a Metal Surface

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Hydrogen bonding has been studied widely over the past decades, an effort that has taken place predominantly in the context of solution—or gas—phase chemistry and in relation to biomolecules.[1,2] Over the past years, an increasing number of adsorbate patterns at solid surfaces have been ascribed to hydrogen bonding interactions, as well.[3–10] Their investigation has remained phenomenological predominantly because obtaining quantitative data on hydrogen bond strengths in the presence of, generally much stronger, adsorbate—substrate interactions is difficult, especially as the latter are at the same time sensitive to the geometry of the adsorption configuration and the local coverage. Theoretical efforts[11,12] show some success, yet there is very little quantitative experimental data available despite increasing interest in complex adsorbate patterns.[13] This paper reports the dynamics and energetics associated with hydrogen bonding based intermolecular interactions of anthraquinone and its sulfur counterpart, 9,10-dithioanthracene, on Cu(111). Our measurements use scanning tunneling microscopy (STM), which by its spatially resolved nature can ensure that all molecules addressed are in equivalent configurations, thus avoiding any impact of surface imperfections.

While in introductory textbooks hydrogen bonding is commonly restricted to hydrogen atoms that are attached to and interact with O, N, or F atoms,[14] research in hydrogen bonding has long recognized that very similar interactions occur in a wide variety of chemical configurations.[1,2] In scanning tunneling microscopy studies, hydrogen bonds have been reported for both the conventional (O,N,F) case and for cases involving, for example, hydrogen atoms of an aromatic ring,[3,10] with the latter kind of hydrogen bonding more commonly reported in low-temperature studies, suggesting—not surprisingly—lower stability for this type of interaction.

Our approach to the energetics of hydrogen bonding at surfaces is derived from measurements of the energetics associated with diffusion, which has been studied for a broad variety of adsorption systems,[15–18] some of which also feature hydrogen bonds. Recent work by the authors established the diffusion barriers E_{diff} of anthraquinone (AQ)[19] and 9,10-dithioanthracene (DTA)[20] on Cu-(111) as 0.023 and 0.13 eV, respectively. These measurements involved recording the rate of diffusion of the molecules at various temperatures, which is subsequently evaluated in an Arrhenius plot.

Both AQ and DTA form rows of molecules on Cu(111), in which the intermolecular interactions stem, at least partially, from hydrogen bonds between the chalcogen atoms of one molecule and the hydrogen atoms of its neighbors,[3] for example, for AQ the O—H—C bond length is 2.8 Å based on density functional theory simulations of the molecular arrangement in the rows.[3] The periodicity and orientation of AQ in the rows are shown in Figure 1; DTA differs from it only by the slightly longer C—S bond compared to a C═O bond. At increased coverage, AQ rows weave into a mesh[3] (Figure 1), whereas DTA rows aggregate into islands of parallel rows.[20] The linear nature of the surface aggregates permits us to obtain information about the energetics of the
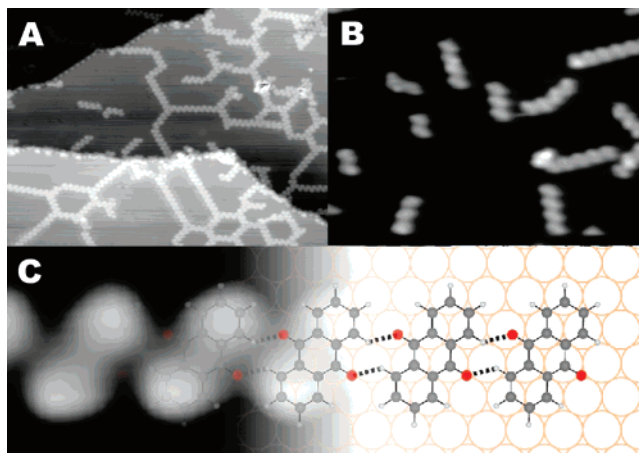

Figure 1. (A, B) STM images of AQ [sample bias = −1.9 V, current = 120 pA, A = 490 Å × 360 Å, T = 103 K] and DTA [sample bias = −1.5 V, current = 230 pA, A = 210 Å × 160 Å, T = 85 K]. (C) Row of individual AQ molecules and the corresponding model (Cu—Cu distance = 2.55 Å). Hydrogen bonds are indicated by dotted lines.
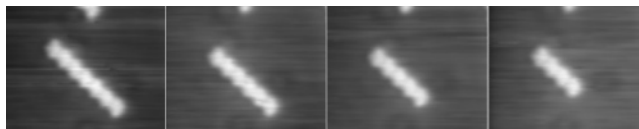

Figure 2. A sequence of STM images showing dissociation of individual DTA molecules from a molecular row (sample bias = −1.7 V, current = 170 pA, A = 90 Å × 80 Å, T = 95 K).
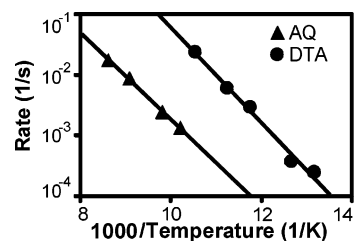

Figure 3. Arrhenius plot of DTA and AQ dissociation from a molecular row. The error bars are smaller than the symbols used. The dissociation barriers are 0.13 and 0.16 eV for AQ and AQ and DTA, respectively.

hydrogen bonding based intermolecular interaction using an experimental approach similar to the investigation of molecular diffusion barriers: temperature-dependent measurement of the rate of abstraction of the terminal molecule from a row of adsorbates. Figure 2 shows one of our experiments; over a duration of several hours, a number of DTA molecules detach from both ends of a molecular row in a consecutive fashion. Based on the abstraction of hundreds of molecules from the ends of AQ and DTA rows on Cu(111) at variable temperature, we calculate the abstraction rate as a function of temperature. This allows us to generate the Arrhenius plot of Figure 3, which reveals a barrier height for
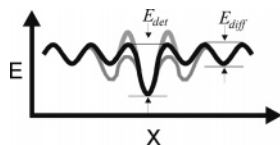
Figure 4. (Black) Schematic of potential experienced by a molecule that diffuses across the end of a row (center). At a lateral distance X to the row terminal, the molecule experiences the diffusion barrier at the substrate periodicity. At the end of the row (center of the graph), an additional attractive interaction exerted by the terminal molecule of the row is present. Simplifications include the possibility of an activation barrier for abstraction from the row end (thick gray curve) and attraction to the terminal molecule of the row even after performing the first step (thin gray curve).

molecular detachment E_{det} of 0.13 and 0.16 eV for AQ and DTA, respectively. Detachment of molecules from within the rows was not observed.

This energy determines the temperature range in which the molecular rows (and the film patterns based on them) are stable and when they start to disintegrate. As such, our measurements provide meaningful information both for the planning of experiments involving patterns of these species as well as for the modeling of pattern formation in a (kinetic) Monte Carlo fashion. Can we also derive information about the strength of the intermolecular hydrogen bonds from our data?

Particular to AQ and DTA on Cu(111) is their propensity for linear diffusion in the direction indicated by their aromatic ring system. Assuming that the detached molecule proceeds, at least for the first few steps, along the preferred diffusion direction indicated by its aromatic moiety (Figure 1), we can approximate the potential energy surface experienced by the detaching molecule as shown in Figure 4, that is, as consisting of a periodic oscillation with the amplitude of the diffusion barrier on the plain terrace and a pronounced minimum at the site of attachment to the row. Under this (simplifying) assumption, the measured detachment barrier represents the sum of the diffusion barrier and the energy associated with the intermolecular hydrogen bonds. Given that there are two hydrogen bonds broken for every detaching molecule (Figure 1), the resultant hydrogen bond energies for AQ and DTA are 0.05 and 0.02 eV, respectively. These values are very low. The key source of error in our measurements is an uncertainty in the temperature calibration by ∼1 K, which associates each of the barriers measured (diffusion and row abstraction for DTA and AQ) with an error of 0.01−0.02 eV. As all measurements involve the same instrument and sample holder, the resultant error is likely to cancel partially. We wish to note, however, that the resultant hydrogen bond energy for DTA is of similar magnitude.

This treatment of hydrogen bonding suffers from a number of poorly justified simplifications. Foremost, it neglects any details of the mechanism by which the molecule detaches from the row (which may involve sequential bond dissociation rather than simultaneous breakage of both). It also omits two antagonistic effects: (a) a potential activation barrier of the abstraction process may increase the observed barrier (upper gray line in Figure 4); (b) less localized, attractive intermolecular interactions may cause an apparent reduction in the barrier toward the nearest neighbor site (lower gray line in Figure 4).

We note, however, that solution-phase measurements indicate very low activation barriers for hydrogen bond scission;[1,2] less-localized effects discussed under (b) are likely to be caused by intermolecular interactions other than hydrogen bonds since the latter require the bond distance and angle to be in a relatively narrow range. Consequently, the effects discussed here may only cause a relatively small deviation of our estimates from the true hydrogen bond energies.

The small absolute value of the hydrogen bonds observed here is not astonishing given that the H-atom involved is attached to an aromatic system rather than to an O, N, or F atom. A difference of a factor of 2−3 in strength between an oxygen-based hydrogen bond and the corresponding sulfur-based one, as observed for AQ and DTA, has been reported for a variety of solution/gas-phase based systems,[1,2] thus lending further credibility to this experimental approach to hydrogen bonding.

Supporting Information Available: Sequence of images showing the dissociation of an AQ chain. This material is available free of charge via the Internet at http://pubs.acs.org.

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