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Atomic-scale chemistry: Desorption of ammonia from Cu(111) induced by tunneling electrons

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Abstract

We report on excitation experiments on individual ammonia molecules adsorbed on Cu(111) using a low-temperature scanning tunneling microscope. Multiple electronic excitation of the ammonia–substrate bond can lead to the desorption of molecules from the substrate and their transfer to the STM tip apex. The dependency of the desorption yield on the tunneling current at different biases shows that the order of the desorption process correlates directly with the minimum number of electrons necessary to overcome the binding energy. In contrast to previous experiments, excitation with *either* polarity, i.e., electron and hole attachment, can cause desorption. Hartree–Fock calculations allow us to deduce from spectroscopical data that the desorption process is mediated by an ammonia modified Cu 4s state near the Fermi level. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Lately, the excitation of individual adsorbates using the scanning tunneling microscope (STM) has gained considerable attention as it opens up new avenues of research and – possibly – application. Desorption of hydrogen from silicon can be induced by vibrational excitation of the adsorbate–substrate bond via inelastic electron tunneling or by electronic excitation of anti-bonding (or depletion of bonding) orbitals. This might eventually lead to industrial patterning processes not limited by optical diffraction in size as lithography [1–3]. For the first time, the elementary processes of bond breaking at surfaces [4–6] and induced rotation of individually designated molecules [7] are directly observed on the atomic scale. Most recently, even vibrational spectroscopy on single molecules was achieved [8]. These experiments improve the microscopic understanding of the mechanisms and dynamics of surface chemistry. They constitute a major step forward towards the long-standing dream of chemists to construct individual molecules from a limited set of building blocks.

Here, we report on the desorption and hopping of individual ammonia molecules on a Cu(111) surface induced by tunneling electrons. This system is of

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particular interest as its surface photochemistry constitutes a simple and well-studied model system for multi-dimensional desorption dynamics [9]. Extensive experimental and theoretical work has been interpreted in the way that desorption induced by UV-photons is mediated by attachment of photogenerated substrate electrons to a Rydberg state of the molecule. This is believed to be able to cause an inversion of the on-top bound pyramidal ammonia molecule (‘umbrella mode’) upon electronic de-excitation to the ground state potential energy surface. Our current study correlates spatially resolved scanning tunneling spectroscopy and electronic structure calculations with the bias (i.e., energy) dependence of the STM-induced desorption process. We find that the desorption can be caused by multiple excitation of the external and – possibly – internal modes of the ammonia molecule normal to the surface. The excitations are caused by electron/hole attachment to the Cu 4s derived density of state (DOS) involved in the ammonia–substrate bond. The order of the desorption process directly correlates to the number of electron/hole energies needed to overcome the desorption barrier at any given bias [10].

2. Experimental

Using a home-built STM operated at 15 K and equipped with tungsten tips [1], we investigate the response of ammonia molecules adsorbed on Cu(111) to the tunneling current. It is found that it is possible to induce ammonia desorption from and movement on the surface using biases as low as 100 mV of *either* polarity. Desorption and translation from/on the surface will be summarized as hopping of the molecule in the following. As the hopping rate turns out to be extremely dependent on the current used, by varying it we could obtain sequences of images in which in an alternating way either the hopping of the molecules was induced or not. To obtain images without causing hopping of the molecules, a gentle set of tunneling parameters like 300 mV bias and less than 0.1 nA current was used. If the hopping of the molecules was desired, substantially higher currents were chosen. Fig. 1a–d shows four images from such a series in which scanning at 2.1 nA current and 450 mV bias was chosen to cause hopping of the ammonia molecules. Clearly, the depletion of ammonia (white dots) from the substrate can be seen.

3. Results and discussion

In Fig. 1e results of several such series obtained at different biases are shown. The charge transferred into a single molecule is estimated from the scanning speed, the current and the size of the protrusions representing the individual ammonia molecules on Cu(111). For the numerical evaluation, only such molecules are considered to be *remaining* which neither desorb *nor move from their initial adsite*. This definition has been used successfully before [6]. It is based on the assumption that apparently laterally moving molecules in fact are backscattered from the tip apex during desorption [11]. In contrast to a previous study, where the desorption of an adsorbed molecule was initiated using only a single polarity [6], here excitation by either polarity leads to a reaction. The dependence of the hopping rate on the applied bias appears to be significantly stronger using negative polarity than positive, as indicated by the large range of slopes shown in Fig. 1e at small variation of the gap bias.

The approximately linear dependence of the logarithm of the number of remaining molecules on the charge q transferred into a single molecule indicates that the depletion of the remaining molecules N is governed by an exponential dependence like $N(q) = N_0 \exp(-q/Q_0)$ typical for an underlying stochastic excitation process. In order to gain more information on the excitation process – especially on the current and bias dependence of the decay constant Q_0 – a better-defined excitation geometry is needed. The tip should be placed at a fixed and well-known position right above the molecule. Because excitation of an ammonia molecule leads frequently to its hopping on the STM tip, which might subsequently change the tips excitation probability, also better care should be

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[1] Although electrochemically etched tungsten tips were used, we expect them to be Cu-covered due to occasional tip–substrate contact during final in-situ tip preparation. Extensive care was taken to prevent tip artefacts in all measurements. Tips used exhibited metallic imaging quality and consistent spectra of the occupied substrate states.

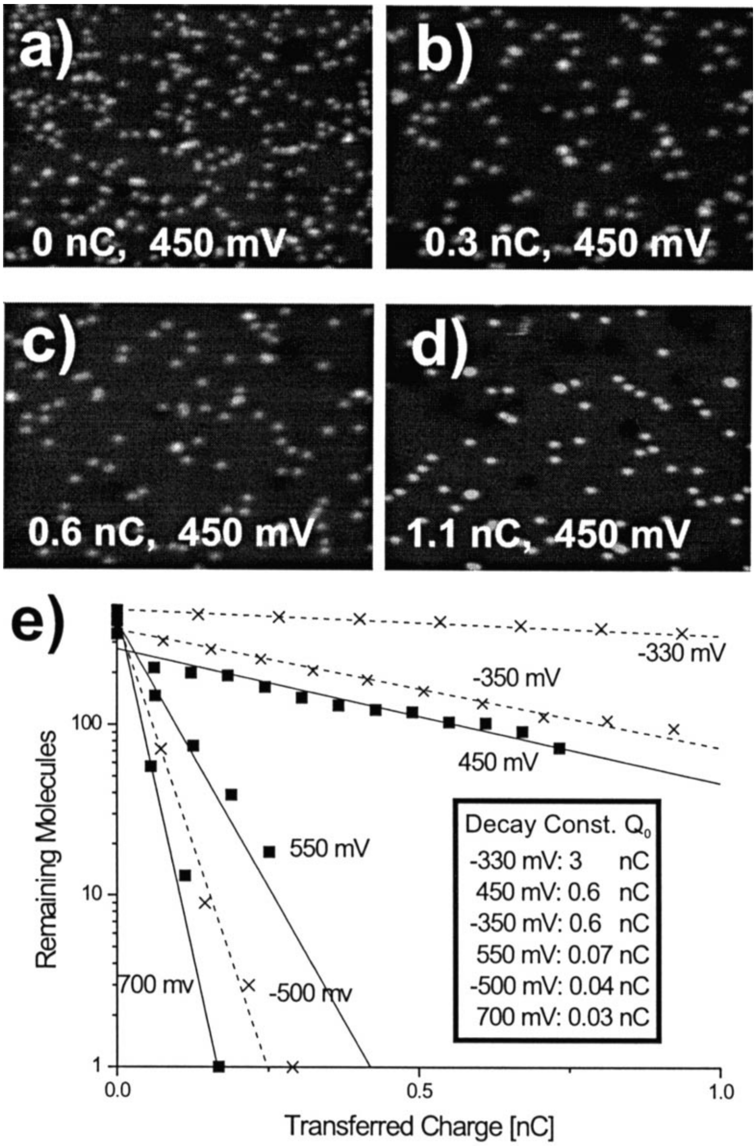

Fig. 1. (a)–(d) Several STM images of the same sample area after subsequent excitation of the adsorbed molecules by scanning with 450 mV bias at a current of 2.1 nA. The number of remaining molecules continously decreases due to induced desorption and several molecules are electronically excited to perform hops on the surface (530×370 Å, 0.1 nA, 300 mV). (e) The number of remaining molecules after introducing the indicated charge into them during scanning at various biases. The exponential decay constants Q_0 are given in the inset.

taken of the tip geometry and composition during the experiment.

An example of an intentional pickup of an NH_3 molecule is given in Fig. 2. The left side shows the tip path while approaching a molecule. At the molecules center the tip movement was arrested and the molecule was excited to hop on the tip. On the right side, the flat path of the ammonia tip above the now undisturbed surface can be seen. Pickup of an ammonia molecule causes the elongation of the tip by almost 2 Å. Such controlled pick-up of molecular species has as yet only been reported for CO [12]

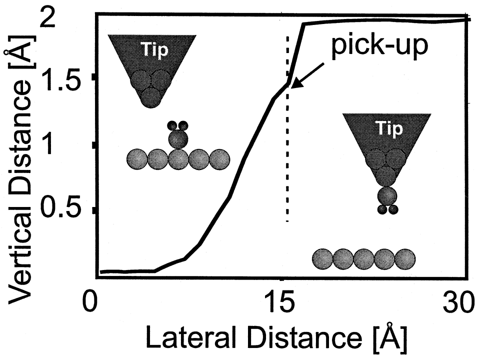

Fig. 2. Height profile during scanning a line in whose center an ammonia molecule is located. Initially starting with a bare tip, at the center of the scan line the tip movement is stopped and the ammonia molecule is transferred to the STM tip apex by decreasing the tunneling gap to increase the current. The second part of the line is scanned with the resulting ammonia tip, which is obviously longer than the initial tip. (Scanning bias: 300 mV; scanning current: 0.1 nA; pickup current: 40 nA).

while it is a familiar process with single atoms [4,12].

Spectroscopy with the STM can be used to distinguish between tips with and without an adsorbed ammonia molecule. Additionally, it also allows to learn more about the molecular levels involved in the excitation process. The upper part of Fig. 3 show two dI/dV spectra of a series acquired at various distances from an NH_3 molecule using the same bare tip apex [14]. In STM the dI/dV signal is a good approximation to the local DOS at the maximum energy of the tunneling electrons [17], i.e., at the applied voltage in eV relative to E_F. When the tip is positioned off the ammonia molecule (solid line) the spectrum is dominated by the decline of the effective DOS of the surface state (SS), which has its band edge at about 400 meV below E_F [18]. The spectrum taken directly at the ammonia molecule (dashed line) differs in the vicinity of E_F: a depletion of the apparent DOS at about 300 mV below E_F and additional DOS above E_F is observed.

It is known from photoelectron spectroscopy that the adsorption of ammonia depletes the SS proportional to the lowering of the work function. This is caused by the ammonia dipole [9]. Thus, a strong depletion of the SS should be found in the spectrum taken at the ammonia molecule. At first glance, however, that seems not to be the case. In theoretical work, Biemolt et al. [15] found that the adsorption of ammonia on copper is governed by the interaction of the NH_3–3σ lone-pair electrons with the substrate 4s and 3d levels. The DOS of the doubly occupied NH_3–3σ level shows pronounced maxima 5–6 eV below E_F consistent with photoemission experiments [19]. Additionally, Biemolt et al. [15] predict a strong influence of the NH_3–Cu interaction on the DOS around E_F. While the overall interaction between the NH_3–3σ level and the 4s valence electrons is bonding, its part associated with the DOS around E_F has a strong repulsive (anti-bonding) character. Consequently, we attribute the features denoted by **I** and **II** in the spectrum in Fig. 3 rather to the ammonia–copper interaction than to the SS, whose possible changes are hidden by it.

Ammonia causes far less oscillation of the Cu(111) SS in its vicinity than, for instance, CO. This might further strengthen the above interpretation of the spectra, as it is based on a strong influence of the adsorption of NH_3 on the substrate 3d and 4s levels. However, it predicts only a negligible effect on the Cu $4p_z$ level [15], out of which the SS is mainly derived [16]. Thus, the SS depletion in photoemission might rather be attributed to changes of the work function and the surface potential caused by the NH_3 dipole [9] than to the chemical substrate bond of the ammonia molecule, which we believe is unable to cause strong scattering of SS electrons into the bulk.

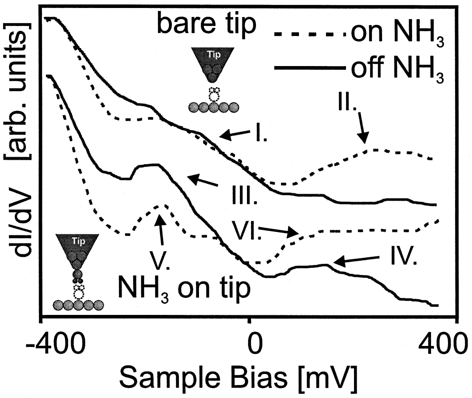

Fig. 3. Top panel: dI/dV spectra acquired with a bare tip off (solid line) and on (dashed line) an ammonia molecule. The ammonia-induced features around zero bias, i.e. at E_F, are marked. Lower panel: Corresponding spectra with a tip bearing an ammonia molecule at its apex are displayed.

Using an ‘ammonia’ tip for spectroscopy far away from any adsorbed molecule (solid line in the bottom of Fig. 3) strong features in the vicinity of E_F reappear. Due to the inverted direction of the current with respect to the molecule, if adsorbed on the tip, an inversion of the superimposed structure with respect to E_F, i.e., compared to the dashed line in the top part of Fig. 3, is expected. However, the difference in geometry of the adsorption site on the Cu tip apex compared to the flat surface may cause additional changes in the spectrum. Keeping this in mind, feature **III** can be identified to correspond to feature **II** found with a bare tip and feature **IV** can be related to **I**. Taking a spectrum at an ammonia molecule – i.e., where the SS is quenched – with an ‘ammonia’ tip the ammonia-related state **I** comes out very pronouncedly (V) due to the extra DOS **III**/**II** on the tip. Also a strong feature **VI** corresponding to the folding of **II** with **IV** is apparent. It shall be noted, however, that while the above arguments seem sufficient for a qualitative description of the spectra, a more detailed analysis of the data must include the precise tunneling probability at any given bias. The latter depends delicately on the interference of partial currents from different states of the tip, adsorbate and substrate and – due to effects of mutual annihilation – is highly non-trivially dependent on the exact local DOS [20].

Given the close proximity of DOS associated with the NH_3–Cu bond to the Fermi edge, it is not astonishing that ammonia can be excited by tunneling electrons at biases as low as 100 mV. In order to obtain quantitative data on the excitation process, the tip was directed right above an adsorbed ammonia molecule, the bias and distance (and thus the current) were adjusted to a fixed value and the time until a hop of the molecule occurred was measured using the simultaneously acquired dI/dV signal.

Fig. 4a shows data obtained at +400 mV (solid line) and −400 mV (dashed line) sample bias and various currents. Error margins where calculated using an exponential fit to the various observed times until a hop occurred. Independent of the polarity, the desorption rate changes approximately quadratically with the applied current. Given the binding energy of about 0.6 eV [10] it is obvious that at a bias of 400 mV a single transferred electron cannot cause desorption. However, a two electron process – as suggested by the quadratic relation between current and desorption rate – is well able to do so [21]. This suggest that using an even lower bias, the desorption process should be of higher order: applying 200 mV of either polarity, the data in Fig. 4b were acquired. In this logarithmic plot the slope of the line connecting the desorption rates at various currents directly corresponds to the order of the desorption process. The observed slope of approximately three is in good agreement with the necessity of three times 200 meV to overcome the desorption barrier of ≃ 0.6 eV. Note, that while at 400 mV sample bias desorption using negative polarity is more efficient, positive polarity is more efficient at 200 mV. This is in good agreement with the data acquired during scanning (see Fig. 1e).

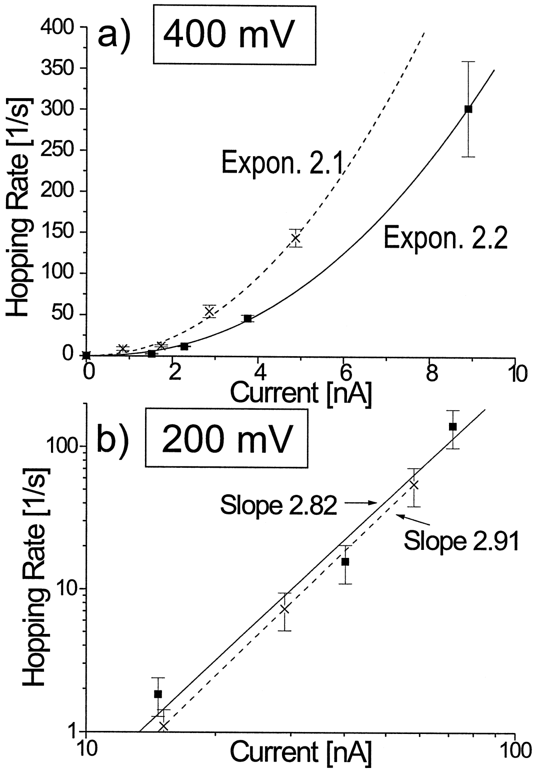

Fig. 4. Top panel: The dependence of the desorption yield on the tunneling current at a bias of 400 mV at positive (solid curve) and negative (dashed curve) sample polarity. The order of the fit functions are indicated. Lower panel: Similar data for 200 mV bias are shown. However, here the *y*-axis has logarithmic scaling allowing for easier comparision of the order of the excitation processs.

Our results indicate that the desorption of ammonia by the tunneling current is governed by a similar process as the dissociation of oxygen on platinum found by Stipe et al. [5]. This mechanism involves vibrational multiexcitation of the adsorbate caused by multiple but subsequent electron attachement to an adsorbate-related electronic state. In the following, we would like to discuss a few details of the excitation process.

Two vibrational modes of ammonia on Cu(111) might bear some relevance for the desorption process observed in this work: the NH_3–Cu mode at 45 meV and the inversion ‘umbrella’ mode at 135 meV [10,22]. Additionally, there are several lower-lying vibrational modes associated with the frustrated lateral translation and tilting of the molecule. Due to their different symmetry compared to the modes normal to the surface, energy transfer between them is extremely inefficient. Therefore, they are unlikely to play a significant role in the desorption process and are omitted from further discussion. The same argument also holds true for anti-symmetric vibrations of the hydrogen atoms. Scattering data by Kay et al. [23,24] suggest that energy transfer between the substrate and inversion mode is very efficient. Indeed, this is supported by model calculations for vibrational coupling using a potential energy surface as described in Ref. [9]. Solving the Schrödinger equation in a two-dimensional model with the nitrogen–substrate bond length and the distance between the hydrogen plane and the nitrogen atom as coordinates, it is found that the energy spacing between neighboring vibrational modes of the same type is strongly decreasing with increasing total vibrational excitation of the molecule. A large number of mixed modes occur, suggesting that the concept of independent, equally spaced normal modes might not be applicable even at low total vibrational excitation of the molecule of less than 1/2 of the energy necessary for desorption [25,26]. This certainly facilitates the multi-excitation process described here, as it allows to find an energetically resonant vibrational mode for a larger number of electron energies.

In the gas phase, threshold resonance measurements by Cvejanovic et al. [27] have shown that electrons of a few hundred meV can cause strong vibrational excitation of ammonia molecules. This provides further support of our assumption that low-energy electrons from the tunneling current are able to cause vibrational excitation. Biemolt et al. [15] calculated that the NH_3–Cu interaction around E_F is repulsive, which suggests that additional population or depopulation of the associated electronic state is very likely to have a strong effect on the equilibrium NH_3–Cu bond length. Thus, by a cycle of (de-) populating this state with the STM current, geometric response of the molecule and subsequent scattering of the electron/hole into the substrate, the molecule might be left in a vibrational excited state just as in the standard MGR/Antoniewicz [28–30] model for electron-stimulated desorption. For sufficiently long vibrational lifetimes with respect to the excitation rate a process of vibrational ‘ladder climbimg’ induced by multiple but subsequent electronic excitations can lead to desorption [21]. To back this up, we performed restricted (open shell) Hartree–Fock cluster calculations and geometry optimization for Cu–NH_3 and its corresponding cation and anion [2]. We find a shortening of the bond length by 4%, respectively 2%. This is well compatible with the calculated displacement between the center of the ground state vibrational mode and the center of the lobe on the metal side of the first excited vibrational state of the NH_3–Cu stretch mode. These findings further supports a model based on the excitation of the Cu–NH_3 stretch mode.

Let us assume that all electronic excitations are due to single electron/hole attachment to the molecule at a time – as generally assumed for the class of processes described by desorption induced by (multiple) electronic transition. Then, a minimum electron energy (i.e., bias) of 135 mV in either direction is necessary to induce an excitation of the umbrella mode and 45 mV for any relevant excitation at all. In contrast to standard electron-stimulated desorption experiments, where monochromatic electrons are used, it is important to note, that in STM measurements at any sample polarity there are electrons transferred at all energies between E_F and the applied bias. At positive sample bias, the largest

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[2] For Cu, the inner 10 electrons were represented by relativistic effective core potentials and high-quality basis sets were used for the valence electrons [31]. N and H were represented by valence double-zeta basis sets.

contribution to the tunneling current stems from tip states close to its Fermi edge, as these electrons have to overcome a smaller potential barrier than those from lower-lying states of the tip (see Fig. 5). This results in a comparatively large fraction of the tunneling current having high energy with respect to the substrate Fermi energy. However, at negative sample bias most of the tunneling current produces holes of low energy in the substrate, as the majority of the current arriving at the tip originates from the Fermi edge of the substrate (Fig. 5). Given this energy distribution in the tunneling current, at positive bias exceeding 135 mV a large fraction of current is able to induce all relevant vibrational excitation. In contrast, at negative polarity, the largest partial current always stems from the regime around E_F of the sample and therefore does not affect the relevant vibrational modes. From this follows, that by increasing the bias from 200 to 400 mV at fixed current, the *increase of the fraction* of the total current, which is able to contribute to the relevant excitations, is far greater for negative sample bias than for positive. This is in agreement with our measurements which show a higher desorption rate at *negative* sample bias at 400 mV and a larger one for *positive* sample bias at 200 mV (Fig. 4). It also indicates that the desorption rate per 'electron/hole of sufficient energy' is larger for hole attachment than for electron attachment. However, whether this is due to a larger partial current through the ammonia-related substrate states at negative polarity compared to positive, or whether it really shows a larger desorption yield per excitation hole attachment, cannot be answered from these measurements. The latter assumption is, however, further backed backed by the calculated larger contraction of the Cu–NH_3 bond for the cation than for the anion.

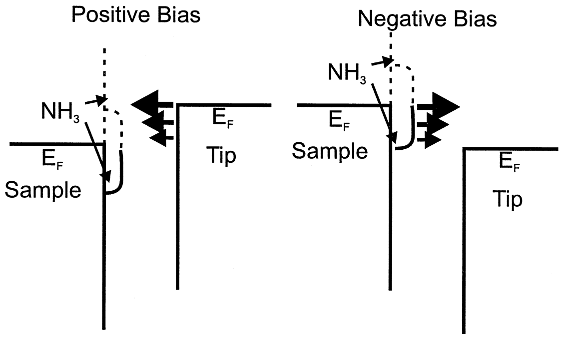

Fig. 5. The difference between the electron energy distribution in the tunneling current of either polarity is visualized. While at positive sample bias (left panel) the majority of the tunneling current stems from states close to the Fermi edge of the tip and thus has comparatively large energy with respect to the sample Fermi level, at negative sample bias (right panel) the majority of the tunneling current stems from states close to the sample Fermi level and thus produces holes of low energy.

Measurements with several hundred nA current at 100 mV bias show a small, but reliable, desorption/transfer yield of ammonia. Assuming that no multi-electron processes occur in the substrate which produce higher-energy electrons, this indicates that a primary excitation of the Cu–NH_3 stretching mode (45 meV) can cause the desorption process – i.e., no direct primary excitation of the umbrella mode is necessary. This is not surprising as the desorption process itself is a process in which the molecule moves exactly along the molecule surface vibrational coordinate. During the multiple subsequent electronic excitations responsible for the vibrational 'ladder climbing', by which the molecule ultimately acquires sufficient energy for desorption, a large number of vibrational states are within energetic reach, that consists of both internal and external vibrational excitation. Thus, an excitation of the umbrella mode might have also occurred by the time of desorption. This would facilitate the adsorption of the molecule on the tip apex, where it is supposed to reside in the standard adsorption position with the nitrogen towards the supporting metal atom. Thus, there is no contradiction to earlier publications [9] on the photodesorption of ammonia, where the importance of the umbrella mode for the desorption process was underlined. As those processes are believed to be caused by a Rydberg excitation of the ammonia, which favors a flat geometry of the molecule, and not by a local net change of charge, as induced here, they might be governed by a different mechanism.

The above discussion is based on the assumption that only a single electronic excitation of the molecule occurs at any time. Given the typical lifetimes of adsorbate states on metal surfaces of a few femtoseconds [6,32,33] anything else would be precluded by the low average rate of transferred electrons: 1 nA corresponds to approximately one electron every 160 ps. It might, however, be questioned whether the electronic state we ascribe the ammonia's excitation to, which is very close to E_F and mainly Cu 4s derived, might truly be compared with the short lived, adsorbate-induced states used or observed previously [5,6]. For a state attributed to a Cu–substrate continuum, Fermi liquid theory would have to be applied resulting in a lifetime depending on the electron energy and, thereby, on the applied bias. For energies just able to excite the Cu–NH_3 stretching mode these lifetimes can be as long as a few picoseconds, thus possibly allowing for coincidental excitation of the molecule by two electrons at currents of a few hundred nA. If the NH_3-modified Cu 4s state is derived from the continuum of the Cu bulk, which is implied by using Fermi liquid theory, then it has to be considered that the 4s derived band approaches E_F away from the bulk Brillouin zone center. The momentum of the electrons prallel to the surface may thus lead to their fast transport away from the adsorption site, making them unavailable for a local double-excitation process. As the STM current is only applied to a point-like area in contrast to photodesorption experiments, energy transport away from the site of excitation can be *in-plane and to the bulk*. This gives rise to several orders of magnitude higher damage thresholds in STM energy transfer than for (fs) laser irradiation. It bears wittness of the high efficiency of the energy depletion off the site of incidence, thus further supporting our assumption of no simultaneous electronic double excitations of the molecule.

Finally, we would like to mention that calculations on the effect of the electric field between tip and substrate were performed on the ammonia–substrate bond. They show that depending on the polarity a strong weakening/strengthening of the bond due to the ammonia dipole can be induced. At fields on the order of a few ten V/nm wavepacket calculations suggest that only minor vibrational excitation of the molecule might cause its desorption [34]. However, in the experiments performed here, the field between the tip and substrate does not exceed 2 V/nm – even including geometric effects. This causes a modification of the binding energy of no more than a few ten meV, below the resolution of our experiments.

4. Conclusion

In summary, we found that STM-induced desorption of individual NH_3 molecules from Cu(111) is possible and can also lead to the transfer of the molecule to the tip apex. This process works independently on the applied polarity, i.e., on whether holes or electrons are injected into electronic states of the molecule–surface bond. The desorption process is attributed to multiple but subsequent electronic excitation via (de-)population of ammonia-modified Cu 4s DOS near the Fermi level.

Acknowledgements

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