Reaction threshold and decoherence: current induced desorption of CO on Cu(111) in STM

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Abstract. The transfer of a CO molecule from the Cu(111) surface towards the STM tip, induced by the tunnelling current, occurs only if a threshold voltage of 2.4 eV is exceeded [1]. We present a theory based on the Quantum Nano Dynamics (QND) approach, treating the competition between a coherent and a decoherent mechanism of current induced CO desorption via inelastic tunnelling and vibrational excitation. The keypoint of the theory is to regard the tunnelling process as driving the system in a transient excited state and to include explicitly many-particle relaxation effects in the excited state. Only a decoherent desorption mechanism via a transient negative ion resonance of the sample surface, which is created through electron injection and interacts with the CO molecule, provides an explanation for the existence of the voltage threshold for CO desorption and reproduces the quantum yield and the isotope effect as observed in the STM experiment.

1. Introduction

In a recent low-temperature STM study Bartels et al. were able to induce the hopping of single CO molecules towards the tip by applying short voltage pulses and tunnelling current from the STM tip towards the CO covered Cu(111) surface [1]. However, the CO transfer was successful only if the bias exceeds a threshold of 2.4 V and then with very low quantum yield of the order of 10\(^{-11}\) per tunnelling electron. Using two-photon photoemission spectroscopy (2PPE) the authors identified the CO induced 2\(\pi\) state at 3.5 eV above the Fermi level and suggested a mechanism for the CO activated desorption relying on the transient population of the 2\(\pi\) negative ion resonance via electron injection from the tip. In a Menzel-Gomer-Redhead desorption picture [2] a monotonously repulsive adsorption potential was assumed for the decohered CO 2\(\pi\) negative ion on Cu(111). Within its lifetime, ranging 0.8-5 fs, the CO negative ion accelerates upon descending the repulsive potential and accumulates the kinetic energy necessary to surmount the activation barrier for desorption on the CO/Cu(111) ground state potential curve.

The physical picture used in the theoretical model of the current induced CO desorption by Hasegawa et al. [3] is that the rate limiting step is the desorption from the potential well of the CO 2\(\pi\)\(^-\) negative ion.

There are some debatable properties of the models based on the assumption that the current induced desorption of CO from Cu(111) is dominated by desorption of the CO 2\(\pi\)\(^-\) negative ion. The most important point is: as it is experimentally established, the 2\(\pi\) resonance of CO adsorbed on a NiAl alloy surface, which has the same band structure as copper, is nearly 5 eV broad [4], having both occupied and unoccupied parts and non-zero spectral weight at the
Fermi level. Therefore, it can be partially occupied even at very low bias voltage, no voltage threshold being necessary for that. An electron decohered in the $2\pi$ orbital will decay in metal continuum states within less than a femtosecond. The core movement of CO cannot be excited within the limited lifetime of the $2\pi^-$ negative ion resonance. Furthermore, the potential curve for adsorption of the $2\pi^-$ negative ion of CO on Cu(111) is very similar to the potential curve for adsorption of CO in its ground state, however, shifted to higher energy by 5-6 eV. In contrast to the repulsive potential assumed by Bertels et al. [1], there exists a potential well for CO $2\pi^-$ adsorption at nearly the same distance between the carbon end and the underlying copper atom, as it is evaluated for the ground state adsorption.

In the present article we propose a new theory of the mechanism of current-induced CO desorption in the STM, based on Quantum Nano Dynamics (QND) [5, 6]. Within 3D scattering theory we study two competing desorption mechanisms for the current induced CO transfer, a coherent and a decoherent one. Only within the decoherent mechanism do inelastic tunnelling and vibrational excitation of the bond between the carbon atom and the copper atom result in CO desorption from the sample surface with a voltage threshold and quantum yield, as they are measured experimentally.

2. QND theory of current-induced CO desorption from Cu(111) in the STM

The Quantum Nano Dynamics theory (QND) of a nanoscopic region embedded in a polarizable medium has been described in recent papers [5, 6]. At this place we focus on the scattering formalism of the current induced CO desorption.

In three-dimensional scattering theory the desorption rate is expressed using the generalized Ehrenfest theorem:

$$R_I = \frac{2\pi}{\hbar} \sum_F \left| \langle F^- | V^{des} | I \rangle \right|^2 \delta(E_{I}^{f} - E_{F}^{f} - \Delta \varepsilon_{vib})$$

with the initial and final states represented as Born-Oppenheimer product states:

$$|I\rangle = |e^{-tip}\rangle |\nu_{CO,chem}\rangle$$

The initial state $|I\rangle$ has the tunnelling electron in a Bloch state in the tip $|e^{-tip}\rangle$ and the CO molecule in the lowest vibrational state of the ground state potential curve $|\nu_{CO,chem}\rangle$. $\Delta \varepsilon_{vib}$ is the energy transferred into the core movement of CO. The final states $|F\rangle$ for the two different desorption paths we discuss will be specified in the next sections, however, the final state of scattering theory $|F^-\rangle$ results from the Lippmann-Schwinger equation:

$$|F^-\rangle = |F\rangle + G^- V^{des} |F\rangle$$

using the Green’s function $G^-$ and the scattering potential $V^{des}$. All quantities needed for the evaluation of the desorption rate result from solutions to the same QND hamiltonian, which is self-consistently solved: the adsorption potential for CO in its ground and ionized state, the scattering desorption-inducing potential and the Green’s function.

The branch ratio is defined as the ratio of the rate of desorption $R^{desorption}$ and the sum of the rates of all processes (desorption and sticking $R^{total} = R^{desorption} + R^{sticking}$):

$$\text{branch ratio} = \frac{R^{desorption}}{R^{total}}$$

Since we have a single tunnelling electron the branch ratio in our model is equivalent to the quantum yield as defined in experiment, i.e. the probability for desorption per incident electron. Therefore we plot quantum yields versus voltage.
2.1. Rate of current-induced desorption in a coherent desorption mechanism

In the coherent desorption path the final states of the system have the tunnelling electron in a bulk Bloch state in the sample and CO is in a unbound continuum state of the CO-Cu(111) potential $|\mu_{CO,free}\rangle$. The scattering potential is the non-adiabatic coupling between the tunnelling electron and the CO core movement, in addition to the interaction potentials of the electron with the tip and the CO molecule with the sample.

\[
|F_{coh}\rangle = |e^{-}\text{sample bulk}\rangle |\mu_{CO,free}\rangle
\]

We refer to this desorption mechanism and its rate as a coherent desorption mechanism and rate. The reason for that will become obvious in a later paragraph.

All physically relevant processes occur in a local region around the potential wells, therefore we introduce a local basis for the representation of the scattering potential and the Green operator. In the case of the coupled electron-core movement the local basis consists of Born-Oppenheimer (BO) product states $\{|B\rangle\}$ which include:

(i) The electron accepting metal negative ion resonance and the CO bound and continuum core movement states in the potential provided by the copper ion resonance.

(ii) The electron accepting CO $2\pi$ negative ion resonance and the CO bound and continuum core movement states in the potential of the CO $2\pi^-$ ion.

\[
\langle F^-|V_{coh}^{des}|I\rangle = \sum_{B,B'} \langle F^-|B\rangle \langle B|V_{coh}^{des}|B'\rangle \langle B'|I\rangle
\]

By including or exempting some basis BO states from the expansion basis set we can evaluate the contributions to the coherent desorption and sticking rates due to the considered basis states. The wave function for the CO core movement in the initial ground state together with the ground state potential are shown in fig. 1 (red curves). One core movement wave function in the final state, belonging to the desorption continuum for the coherent mechanism, is shown as well. The initial and final state wave functions are solutions to the same potential for the CO core movement.

2.2. Rate of current-induced desorption in a decoherent desorption mechanism

The desorption mechanism described so far is the standard description of scattering theory based on the fundamental axioms of quantum mechanics. The system is prepared at time $t = 0$ in a given initial state $|I\rangle$, then its time evolution is governed by the time-dependent Schrödinger equation till time $t$, when it is measured. This mechanism and its formal description we call coherent mechanism, because in the time interval from 0 to $t$, when the measurement is performed, the system evolves coherently according to the time-dependent Schrödinger equation.

In contrast, in a decoherent desorption mechanism the system arrives at its final state stepwise by decohering into subsequent transition states. The desorption rate is limited by the rate of the slowest step, which in our model we postulate to be the transition from the initial state to a transient negative ion resonance on the metal surface $|e^-_M\rangle$ (MNIR), produced when the tunnelling electron is injected from the STM tip. The motivation for this choice is the existance of a directional band gap along the [111] direction of fcc copper which is a warrant for an energetically very sharp ion resonance within the gap. Hence, its lifetime is long enough for the environment to decohere the electron in the metal negative ion resonance. This is the final state in the decoherent desorption mechanism we consider:

\[
|F_{decoh}\rangle = |e^-_M\rangle |\mu_{CO,excited}\rangle
\]
Figure 1. One-dimensional potential for CO core movement in its ground electronic state (red dashed curve) between Cu(111) and the tip electrode, a single Al atom adsorbed at its equilibrium position on the Al(111) surface. The tip is 20 a.u. away from the sample surface. Two core movement wave functions are also plotted: for the initial ground vibrational state and for one final desorption state in a coherent desorption of CO (red full curves). One-dimensional potential for CO core movement provided by a negative ion resonance on the Cu(111) surface (blue dashed curve), which is transiently created by electron injection from the STM tip in a local area on the sample facing the tip atom. One final core movement state for decoherent desorption of CO, belonging to the continuum of desorption states, is represented with a blue full curve.

with \{ | \mu_{CO,excited} \rangle \} the set of bound and continuum core movement states for CO in the potential provided by the negative ion resonance on the underlying copper atom in Cu(111). The scattering potential \( V_{\text{des decoh}} \) is defined by:

\[
V_{\text{des decoh}} = W_{\epsilon_m - \text{tip}} + W_{\epsilon_m - \text{CO}} + W_{\epsilon_m - \text{sample}}
\]

all interaction potentials, which are switched off when the tunnelling electron is decohered in the negative ion on the copper surface.

The potential for CO core movement provided by the transient MNIR is plotted in fig. 1 with a blue dashed curve. One final state wave function for the CO core movement, eigenfunction of this potential with energy equal to 2.7 eV, is also displayed (blue full curve).

3. Results

The quantum yields for desorption along the coherent desorption path are displayed in fig. 2 with blue and green curve if the expansion basis in eq. 7 contains the CO \( 2\pi \) or the metal negative ion resonance, respectively. Summarizing:

(i) There is no voltage threshold for CO desorption. The voltage of 0.6 V where the two curves start deviating from zero is just the activation energy for CO extraction out of its ground state potential well on Cu(111). However, this value has nothing to do with the measured value of 2.4 V.

(ii) The theoretical quantum yields are 1-2 orders of magnitude smaller than the experimental values.

(iii) The coherent desorption via the metal negative ion resonance dominates at voltage lower than 2.8 V, above 2.8 V desorption via the CO \( 2\pi \) negative ion resonance dominates.
trend correlates with the projections of the different tip orbitals on the sample, i.e. the electron giving orbitals are projected on the sample states. The larger the projection, the larger the probability for injecting the electron into the sample. The copper negative ion resonance will arise when an electron is emitted from the 3s and 3p<sub>z</sub> orbital on the Al tip atom, whereas a 2π<sup>-</sup> CO will be created when the electron is emitted via the 3p<sub>x</sub> and 3p<sub>y</sub> tip orbitals. The probability for creating the Cu negative ion resonance is larger at energies lower than 2.8 eV and therefore the desorption yield at \( U < 2.8 \text{V} \) via the copper negative ion dominates.

![Graph showing quantum yields versus voltage for CO desorption from Cu(111) tip Al/Al(111)](image)

**Figure 2.** Quantum yields versus voltage for coherent desorption via CO 2π negative ion resonance (blue curve) and via metal negative ion resonance (green curve). Quantum yields versus voltage for decoherent desorption via metal negative ion resonance (black dashed curve). The total quantum yield for all desorption processes is plotted with a red curve.

Why is there no voltage threshold for the coherent desorption mechanism? The answer is: because the initial and final states are on the same potential curve. The only threshold which has to be surmounted then is the energy for CO desorption in the ground state which equals 0.6 eV. The reason for the low quantum yields in the coherent desorption mechanism is the interference cancellation of the contributions from the different desorption routes due to definite phase relations.

To solve the problem we utilize the idea of a decohered intermediate state in the time evolution of our system. Even if the system has to evolve further with time, once in the decohered state, it has to start its coherent time evolution anew. When decoherence occurs the system is on a way of no return, i.e. the CO molecule will desorb with unit probability. In our model this is the final state and we do not treat the further development. Capture of the electron in the later on
decohered ion resonance is the rate determining step of the whole desorption process. A rough estimate of the decoherence rate of large molecules in air is $10^{-14}$ s, hence a very fast process compared to the time scale of $10^{-10} - 10^{-11}$ s for electron delocalization out of a localized state in a band gap. What does that imply for the decoherent CO desorption mechanism? It implies that if an electron has decohered in a negative ion resonance state, the CO core movement is automatically decohered.

The only negative ion resonance, which has a sufficiently long lifetime, is created when the tunnelling electron is injected in a local area on the sample facing the tip. A metal negative ion resonance (MNIR) on Cu(111) is created locally and transiently as the electron accepting state. It is generated by the superposition of the most diffuse unoccupied surface state components on the copper (111) surface, which is known to have a directional band gap at the center of the Brillouin zone. The potential for CO movement, when the tunnelling electron is decohered in the MNIR, has a local minimum and a barrier for desorption, as it is shown by the blue dashed curve in fig. 1. With the CO molecule far from the Cu(111) surface the MNIR lies near the Fermi level. However, when CO approaches the surface the potential turns more repulsive due to the repulsion with the electron trapped in the MNIR. At closer distance the quantum mechanical interactions between CO and the rest system, the MNIR included, lead to the potential well for CO adsorption.

The quantum yield in the decoherent desorption process is zero for bias voltage below 2.5 eV, as it can be seen in fig. 2 (the dashed black curve). The total quantum yield for desorption along all routes we are discussing is plotted with a full red curve in fig. 2. For bias voltage above the threshold the theoretically evaluated total quantum yield rises more than two orders of magnitude, reaching the value of $4 \times 10^{-10}$, which compares nicely with the experimentally determined value of $3 \times 10^{-11}$ per electron. Similar plots for the two isotopes of carbon monoxide are displayed in fig. 3. The ratio of the quantum yields for the two isotopes equals 1.5 in the present theory, the experimentally determined value being $2.7(\pm 0.3/ - 0.5)$. Thus via the decoherent desorption of a CO molecule, induced by a single tunnelling electron in the STM, we reproduce both the existence and the value of the voltage threshold, as well as the magnitude of the quantum yield and the isotope effect, as they are reported by Bartels et al. from their STM experiment [1].

What is the physical reason for the voltage threshold in the decoherent desorption mechanism? The voltage threshold is just the activation barrier to be surmounted by the CO molecule, adsorbed in its ground electronic state on Cu(111), to reach the top of the desorption barrier of the potential, provided by the metal negative ion resonance.

Our desorption mechanism relies on the creation of a metal negative ion resonance on the Cu(111) surface and requires a sufficiently long lifetime of the MNIR. A competing process, which will reduce the lifetime and hence will hinder electron decoherence in the MNIR, is the escape of the tunnelling electron into bulk Bloch states. In the case of Cu(111) the metal negative ion decays slowly because it lies in a band gap centered at the $\Gamma$ point. Since the metal negative ion resonance is very diffuse in position space, in momentum space it is very contracted and does not couple efficiently to extended metal Bloch states of high parallel momentum. The MNIR is generated mostly from the unoccupied surface state components Cu(111). Many different experiments and theoretical considerations give evidence of its long lifetime on the (111) faces of fcc Cu and Ag [7, 8, 9]. Therefore, an electron trapped in the MNIR will have sufficiently long lifetime to allow the interactions with the environment to decohere it. In contrast, decoherence in the $2\pi^-$ CO negative ion resonance is less probable, because the $2\pi^-$ ion is less diffuse in momentum space and it lies lower in the gap, where the gap is narrower. Therefore electron escape from $2\pi^-$ is more probable than from the MNIR and decoherence of the tunnelling electron in CO $2\pi^-$ is less probable. Another way of saying this is: since the $2\pi^-$ is a broad resonance with spectral weight at the Fermi level, there are infinitely many $2\pi$-ion potential
energy curves starting from the ground state potential, decoherent transition in the $2\pi$ would not explain a voltage threshold. To the contrary, the potential energy curve for CO movement in front of the metal negative ion resonance is the lowest out of a whole family of curves.

In the theory proposed by Hasegawa et al. the decoherence of the tunnelling electron in the $2\pi^-$ ion resonance is the major assumption [3]. Furthermore the core movement potential is assumed identical for the ground state and the ionized electronic state of CO and the interaction between CO $2\pi$ and the metal states is parameterized and fitted in a way to reproduce the experimentally observed low desorption yield. Contrary to the model suggested in ref. [3] all quantities used for the evaluation of the desorption rates in our theory result from the solution of the same hamiltonian which provides the potentials for the core movement, the scattering potentials for desorption, the Green’s functions [10].

4. Conclusions
We discuss two competing desorption mechanisms for the current induced CO transfer from the sample towards the tip, a coherent and a decoherent one, via inelastic tunnelling and vibrational excitation of the C-Cu bond. The decoherent mechanism is the only one which reproduces all experimental observations: the existence of the voltage threshold, the quantum yields of the desorption process and the isotope effect. The keypoint of this mechanism is to regard the tunnelling process as electron injection in a relatively local region on the sample, driving the system in a transient excited state, in which the tunnelling electron is decohered in a diffuse negative ion resonance on the sample surface. The negative ion resonance is very sharp, because it lies energetically in the band gap, typical for Cu(111) at the $\bar{\Gamma}$ point. The lifetime of the metal negative ion resonance is sufficient for the excitation of the CO core movement.

The ion resonance picture has been successful in elucidating many phenomena in the STM and AFM on clean and adsorbate covered metal surfaces: the high corrugation amplitudes on metal surfaces at normal tunnelling conditions, the origin of STS structures which are not seen in other surface sensitive spectroscopies, the tip-dependent contrast in STM of adsorbates, the nature of the long-range forces in AFM [5, 6].

5. References
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