Revealing reaction kinetics on gold surfaces by chemically induced tunnel currents

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Our work
- Studying electronic excitation processes in the course of adsorption, chemisorption and surface reactions
- Understanding the role of single reaction steps in the entire process of chemically induced electronic excitation
- Determination of the excitation energy

Methods
- Detection of electronic excitation as tunnel current with 0 V tunnel bias in thin metal-insulator-metal junctions
- Characterisation of reaction kinetics by guiding a bunch of atoms or molecules on the surface
- Energy selective detection of the electronic excitation by the application of a bias tunnel voltage
- Comparison of chemically induced excitations with photo excitations

Experimental Setup

Layer system:
- 30 nm thick tantalum evaporated by e-beam
- 3.4 nm amorphous tantalum oxide produced by local electrochemical oxidation. Thickness adjustable to +/- 0.2
- 15 nm thick gold film in situ prepared in UHV, oriented

Experimental results
Possible sources of the signal

In the course of adsorption and LH reactions

Energy selective detection of e-h pairs
In the course of adsorption and HA-ER reactions

Chemically induced tunnel current as a function of sample temperature

» Simple square form for temperatures T > 250 K

Theoretical consideration

\[
J_{\text{excitation}} = A \cdot \exp \left( -\frac{\beta (E - E_0)}{k_B T} \right)
\]

- \(J_{\text{excitation}}\) taken to be Maxwell distribution
- \(\beta\) exactly founded by TDDFT calculations by group E. Pehlke

\[
A = 1 \cdot 10^{-6}
\]

- \(T = 1000 K\)

- band gap = 4.0 eV

- barrier height = 2.0 eV

Small influence of the bias voltage on deuterium induced signal
- wider distribution of excited electrons for D than for H

Some reaction kinetics

Atomic adsorption

\[
\text{H} + \text{H}_2 \rightarrow \text{H}_2(\text{ad}) + \Delta E
\]

Langmuir-Hinshelwood reaction (LH)

\[
\text{H}_2(\text{ad}) + \text{H}_2(\text{gas}) \rightarrow \text{H}_3(\text{gas}) + \Delta E
\]

Eley-Rideal reaction (ER)

\[
\text{H}_2 + \text{H}_2(\text{gas}) \rightarrow \text{H}_3(\text{gas}) + \Delta E
\]

Hot atom Eley-Rideal reaction (HA-ER)

\[
\text{H}_2(\text{gas}) + \text{H} \rightarrow \text{H}_3(\text{gas}) + \Delta E
\]

Incident H-atom sample at simple surface sites before reacting with an accommodated H-atom

Change of polarity in the H induced tunnel current indicates:
- a simultaneous detection of electrons and holes
- a detection method which acts as an two band tunnel device

Capillary induced photocurrent plays minor role
- Tunnel current induced by H atom impact