Electronic excitations and surface chemistry

One of the hottest fields in surface chemistry is the femtochemistry in which absorption of a fs light pulse creates a non-equilibrium distribution of hot electrons that may be characterized by a much higher temperature $T_{el}$ then the temperature of the phonon bath $T_{ph}$ and of the adsorbates $T_{ad}$.

The chapter analyzes:
1) Surface reactions causing electronic excitations
2) Controlled surface excitations leading to surface reactions

Molecular reactions causing electronic excitations are often associated with light emission called chemiluminescence.

Typical relaxation times:
For electronic excitations $10^{-15}$ s
For phonon emission $10^{-8}$ s
Chemiluminescence

Example: agglomeration of Ag and Cu in rare gas matrixes

The noble metal atoms migrate and agglomerate into small clusters which eventually coalesce into larger ones. The gain in binding energy may lead to the ejection of electronically excited fragments.

The relevant clusters for Ag are of some 10 to 20 atoms, whose bonding still corresponds to localized molecular orbitals. Above that size the bonding is described by a delocalized electron gas with lifetimes of the excited states in the fs range.

*FIGURE 4.1.* Agglomeration of Cu or Ag atoms in a noble gas matrix leads to electronically excited clusters that eject fluorescing atoms or dimers.
Chemiluminescence

**FIGURE 4.2.** The spectra of light emitted from Cu$_2$ in a Ne matrix (a) and of Cu atoms in an Ar matrix (b) [3].
Exoelectron emission

Langmuir and Kingdon noticed that thermal desorption of Cs from W occurs in form of Cs$^+$ ions.
Reason: → stripping an electron off the Cs atom costs 3.9 eV, transferring it to W allows to gain 5 eV

Haber and Just reported that reaction of oxygen and other electronegative molecules with alkali metal surfaces causes emission of electrons (exoelectrons)

Low energy cut off caused by the work function change.

For fixed work function value there would be no increase in the electron yield.

\[ \text{FIGURE 4.3. Emission of exoelectrons upon interaction of O}_2 \text{ with a Li surface [9]. (a) Electron intensity as a function of O}_2 \text{ exposure. (b) Variation of the work function with O}_2 \text{ exposure. (c) Kinetic energy distributions of the emitted electrons at three stages marked in (b).} \]
Exoelectron emission

Upon approaching the surface the affinity level lowers until it crosses the Fermi level of the surface.

When this happens it is occupied by electron tunneling (harpooning) and the so created negatively charged ion is accelerated to the surface where the chemical bond is established.

Alternatively the molecule remains neutral and the affinity level lowers further. When the energy is finally released it is removed via the Auger effect. Since the valence band is involved the distribution of the emitted electrons spans from the work function to $\varepsilon_A$.

The process involves non-adiabaticity and is thus more likely for swift molecules. Photon emission possible but less probable.

2000 m/s = 0.2 nm in 100 fs
Chemicurrents

Exoelectrons have to overcome the workfunction and were indeed observed only for low work function metals.

A more efficient manifestation of electronic excitations caused by chemical reactions are thus chemicurrents.

The system acts as a diode. Electrons with excitation energies >0.8 eV can pass into the semiconductor and be detected as a current.

The efficiency is about 1 e\(^{-}\) per 1000 adsorption events. The device works as a sensor for CO using CO oxidation.
Electron stimulated desorption (ESD)

Irradiation of an adsorbate covered surface may cause desorption of positive as well as negative ions, an effect known as Desorption induced by electronic transitions (DIET).

Menzel-Gomer-Readhead mechanism: Frank Condon transition from the ground state to an excited state where during the short lifetime the adsorbate or one of its fragments may escape from the surface.

Alternatively (Antoniewicz mechanism) the positive ion is attracted towards the surface by its image charge, reneutralized by the contact with the metal and emitted in the neutral state (see figure).
Angle resolved ESD (ESDIAD)

**PF₃ at Pt**

Electron bombardment of isolated molecules gives rise to F⁺ emission with a peak energy of 4 eV for electron energies > 26.5 eV.

For thick adlayers also P⁺, PF₂⁺ and F⁻ are observed
Angle resolved ESD (ESDIAD) with STM

ESDIAD has been observed also for single molecules with STM. E.g. OH disruption on Ag(110)
Angle resolved ESD (ESDIAD) with STM

The energy can move to other modes: acetylene /Cu(100) excitation of the CH stretch at 358 eV leads to a 10 fold increase of the rotation rate. Desorption of ammonia on Cu(100) can be induced by exciting either the stretch or the inversion vibration.

**FIGURE 4.9.** Rates for desorption and C–Cl bond dissociation for chlorobenzene adsorbed on Si(1 1 1) as a function of the current between the STM tip and the surface [59].
CO hopping from the surface to the tip can be induced by bias voltages exceeding 2.4 eV.

Two photon photoelectron spectroscopy (2PPE-femtosecond time resoltion) revealed that the process involves the transient population of the CO $2\pi^*$ derived level at 3.5 eV above $E_F$.

The DIET mechanism results in a probability of $5 \times 10^{-9}$ per photon because the residence time of the electron is $<5$ fs:

**Lowest limit of the timescale of chemical processes**

*FIGURE 4.10. The mechanism of desorption of CO adsorbed on Cu(1 1 1) by electrons from an opposite STM tip by which the CO-$2\pi^*$-derived level is transiently populated [60].*
FIGURE 4.11. Energy diagram for an adsorbate covered metal surface under the influence of light absorption.
Example: Photodesorption of ammonia (NH$_3$) off Cu(111)

1) Laser excitation from ground state minimum.
2) System lands on repulsive excited state potential.
3) H atoms of ammonia start to bend down and umbrella mode is excited in MGR mechanism.
4) Some molecules gain enough energy to desorb. Desorbing molecules are vibrationally excited.

FIGURE 4.12. Photodesorption of ammonia from a Cu(111) surface. Model potential energy surfaces for the ground state and the excited state, respectively, as a function of the coordinates $x$ and $z$. The lower part shows a contour plot of the ground-state PES and the solid line displays a typical desorption event on a calculated trajectory that had spent 9 fs on the excited-state PES [65].