Nitrogen atoms and molecules landing, reacting, and rebounding at metal surfaces

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Outline

1. Introduction to dynamics at gas/solid interfaces
2. Methodology. Non-adiabatic effects
3. Reactivity at strained surfaces
4. Reactivity and direct pick-up of atoms at surfaces.
Gas – solid interfaces
physics and chemistry at surfaces

from the fundamental point of view, the goal is to understand how solid surfaces can be used to promote (or inhibit) gas-phase chemical reactions: HETEROGENEOUS CATALYSIS
Why are surfaces so good catalysts?

Dissociation is in many cases the limiting step

\[
\begin{align*}
\text{N}_2 & \quad E_{\text{diss}} \approx 9.8 \text{ eV} \\
\text{NO} & \quad E_{\text{diss}} \approx 6.5 \text{ eV} \\
\text{O}_2 & \quad E_{\text{diss}} \approx 5.1 \text{ eV} \\
\text{H}_2 & \quad E_{\text{diss}} \approx 4.5 \text{ eV}
\end{align*}
\]
heterogeneous catalysis in industry

chemical industry

surfaces used as catalysts in many industrial processes

catalytic converters reduce toxic emissions by promoting reactions at catalytic surfaces

aerospace industry

thermal shielding for the reentry of space shuttles (CNES / Aquitaine)
nitrogen chemistry

the nitrogen molecule is extremely difficult to break

\[ N_2 \quad E_{\text{diss}} \approx 9.8 \text{ eV} \]
\[ NO \quad E_{\text{diss}} \approx 6.5 \text{ eV} \]
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binding energy \( \sim 9.8 \text{ eV} \)
one of the strongest in Nature!
reactivity can drastically change with atomic-level modifications

defects & vacancies

Details of the surface electronic structure can largely change the reactivity: $\text{N}_2/W(110)$ and $\text{N}_2/W(100)$.
why $\text{N}_2$ abundantly dissociate on $W(100)$ and not on $W(110)$

Alducin et al., PRL 97, 056102 (2006); JCP 125, 144705 (2006)
Picosecond dynamics of atoms and small molecules at surfaces: methodology

1.- Ab-initio molecular dynamics (AIMD), with forces calculated on-the-fly.

2.- Building a potential energy surface (PES) and performing molecular dynamics on it:

- PES based on $10^3$-$10^4$ ab-initio (DFT) points.
- adiabatic approximation
- frozen surface
- interpolation of the DFT data, corrugation reducing procedure (CRP)
Picosecond dynamics of atoms and small molecules at surfaces: methodology

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Classical trajectory calculations:
Monte Carlo sampling of initial conditions
non-adiabatic effects: electron-hole pair excitations

chemicurrents

vibrational promotion of electron transfer

friction of a single chemisorbed CO molecule

NO on Cs/Au(111) electron emission as a function of initial vibrational state

CO on Pt(997) migration to step edges

Huang et al., Science 290, 111 (2000)
White et al., Nature 433, 503 (2005)

Gergen et al., Science 294, 2521 (2001)
Hagemann et al., PRL 104 028301 (2010)

Takaoka et al., PRL 100, 046104 (2008).
description of electronic excitations by a friction coefficient

previously used for:
- damping of adsorbate vibrations:
  Persson and Hellsing, PRL49, 662 (1982)
- dynamics of atomic adsorption
- dissociation dynamics (low dimensions)
  Luntz et al., JCP 123, 074704 (2005)

classical equations of motion

for each atom “i” in the molecule

\[ m_i \frac{d^2 r_i}{dt^2} = -\frac{dV(r_i, r_j)}{dr_i} - \frac{\eta_i}{d} \frac{dr_i}{dt} \]

adiabatic force:
6D DFT PES

friction coefficient:
fraction coefficient: effective medium approximation

bulk metal

\[ n(z) \]

\[ n_0 \]

\[ \eta = n_0 k_F \sigma_{tr}(k_F) \]

effective medium:
FEG with electronic density \( n_0 \)

Juaristi et al., PRL 100, 116102 (2008)
energy dissipation channels: phonon excitation

- S. A. Adelman

- John C. Tully

- H. F. Busnengo et al.
Energy loss of reflected molecules: N$_2$ on W(110)

**Experimental conditions**

- $T_s=1200$K
- $T_{rot} < 5$K (J=0)
- Normal incidence and detection

![Experimental data by Hanisco et al.](J.Vac.Sci.Technol. A 11, 1907 (1993))
Energy loss of reflected molecules: N\textsubscript{2} on W(110)

Experimental conditions

- $T_s=1200\text{K}$
- $T_{\text{rot}}<5\text{K}$ (J=0)
- Normal incidence and detection

Experimental data by Hanisco et al. 

- adiabatic
- electronic friction
- phonons
- phonons + friction

Phonon excitations are responsible for most of the energy transfer observed experimentally.

Martin-Gondre et al., Comp. and Theoret. Chemistry 990, 126 (2012).
reactivity can drastically change with atomic-level modifications

Does the reactivity of N\textsubscript{2} increase in strained Fe monolayers?

Fe(110)  Fe/W(110)

Fe monolayer grown on W(110) is expanded \approx 10\%
Does the reactivity of N$_2$ increase in strained Fe monolayers?

N$_2$/Fe(110) vs. N$_2$/Fe/W(110)

20 ML Fe(110) = bare Fe(110) = no N$_2$ adsorption

1 ML Fe/W(110) = N$_2$ adsorption!

Molecular adsorption dynamics

$N_2/Fe(110)$

$N_2/Fe/W(110)$

PW91: 14 meV

150 meV

50 meV

0 meV !!


I. Goikoetxea et al. (submitted)
Why $N_2$ adsorbs more on Fe/W(110)
Projected Density of States (PDOS)

$N_2$/Fe(110)  $N_2$/Fe/W(110)

I. Goikoetxea et al. (submitted)
Why $N_2$ adsorbs more on Fe/W(110)
Projected Density of States (PDOS)

The energy difference between the molecular orbital $\Pi_g^*$ and the d-band center is much reduced in Fe/W(110)
Why $N_2$ adsorbs more on Fe/W(110)  
Projected Density of States (PDOS)

$N_2$/Fe(110)

$N_2$/Fe/W(110)

minority-spin electronic charge transfer from W to Fe

spin down

2.53$\mu_B$/atom

2.74$\mu_B$/atom
the unexplored regime: hyperthermal atoms and molecules

Effusive beams:
atoms $<E_i> = 4.3 \text{ eV}$
molecules $<E_i> = 5.6 \text{ eV}$

$Q_i = 60^\circ$

$\Theta_i$ and $\Theta_f$

$N, N_2$ and $E_i$

$\text{metal surface}$

$\text{Distribution of atomic energies in the effusive beam}$

fwhm = 5.6 eV

$<E_i> = 4.3 \text{ eV}$


Clean Ag(111) vs. N-covered Ag(111) molecular N\textsubscript{2} scattering (effusive beam)

Signal of N\textsubscript{2} molecules is higher in the N-covered surface

Clean Ag(111) vs. N-covered Ag(111) molecular N$_2$ scattering

**Question**: why the signal of N$_2$ molecules (at low angles) is higher in the N-covered surface?

**Answer from DFT-based calculations**:

Energy ratio at low final angles $<E_f>/<E_i>$ should be *different*!
Clean Ag(111) vs. N-covered Ag(111) molecular N$_2$ scattering

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Is the direct pick-up of N adsorbates by gas-phase N atoms possible? Is it efficient enough?

\[ \frac{\langle E_f \rangle}{\langle E_i \rangle} \]

\[ \text{Exp. Clean} \quad \text{Exp. Covered} \quad \text{Theo. Covered} \]

\[ 0 \quad 20 \quad 40 \quad 60 \quad 80 \]

\[ \Theta_f (^\circ) \]

\[ 0.6 \quad 0.8 \quad 1.0 \quad 1.2 \quad 1.6 \]

\[ \text{GLO} \quad \text{Adiabatic} \]

\[ \# N_2 / \# N \text{ projectiles} \]

\[ 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \]

\[ \text{effusive beam} \quad > 35\% \text{ efficiency} \]

Blanco-Rey, et al., (submitted)
Is the direct pick-up of N adsorbates by gas-phase N atoms possible? Is it efficient enough?

Blanco-Rey, et al., (submitted)
In summary:

- DFT-based molecular dynamics are accurate tools to describe, predict, (and understand!) the dynamics of atoms and small molecules on surfaces.

- Current challenge is the inclusion of non-adiabatic and dissipation effects in the dynamics.

- Dynamical processes are quite sensitive to small changes in the electronic and structural details of the surface. Unexpected effects going beyond general trends are often found.
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thank you for your attention
Further reading:

Dynamics of Gas-Surface Interactions
Atomic-level Understanding of Scattering Processes at Surfaces


Edited by Ricardo Díez Muiño and Heriberto Fabio Busnengo