Surface Reactions induced by XUV Laser Radiation

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Introduction

Reaction dynamics on interstellar dust particles

horsehead nebula

protoplanetary disc
Introduction

Reaction dynamics on interstellar dust particles
molecular hydrogen formation (Salpeter, 1963, 1970)

Dust particles: graphitic, olivines, ice-covered (H$_2$O, CO, CO$_2$) cores

formation of H$_2$ on amorphous ice/graphite:

Photon-induced reactions
desorption of H atoms, formation of H$_2$, CO, H$_2$O, CO$_2$, NH$_3$
Introduction

Femtosecond hot electron induced reactions:

**laser desorption:**  
NO / Pd(111), O₂ / Pt(111)  
CO / Pt(111)  
CO / Cu(111)  
NO / NiO(100)

T.F. Heinz and coworkers, PRL, 64, 1537 (1990)  
F. Budde et al., PRL, 66, 3024 (1991)  
F.J. Kao et al., PRL, 71, 2094 (1993)  
L.M. Struck et al., PRL, 77, 4576 (1996)  

**laser induced diffusion:**  
O / Pt(111); CO / Pt(111)

J. Güdde et al., PRL, 94, 236103 (2005)  
M. Bonn and coworkers, Science 310, 1790 (2005)

**laser induced reactions:**  
O + CO / Ru(0001)  
D + D / Ru(0001)

D.N. Denzler et al., PRL, 91, 226102 (2003)  

metal substrates and large band gap systems

electronic excitations are central
nearly all experiments on **metallic surfaces**

**low-lying excitations:** near IR wavelength of the inducing laser

**two-temperature model** for electron and phonon excitation

**electronic friction** for electronic coupling to the adsorbate molecules

**Introduction**

-indirect ~30fs

-direct

~ 0.1 - 1 ps

> 1 ps

-electrons, excitons $T_{el}$

-adsorbate film $T_{ads}$

-phonons $T_{ph}$

Substrate: metals, semiconductors, insulators
Three temperature model

\[ R(t) \propto E_a \int_0^\infty dt \frac{\eta}{T_{ads}} e^{-E_a/(k_B T_{ads})} \]

Reactions of molecules and atoms at surfaces at high photon energies:

- substrate mediated
- direct excitation of the adsorbate
- excitation of the substrate – adsorbate complex
- participation of inner shell states

Model systems: NO / graphite; H (D) / graphite
Graphite with NO

$E_{\text{vac}} = 0 \text{ eV}$

$E_F = -4.5 \text{ eV}$

-8.5 eV

-9.24 eV

$\pi$

$\sigma$

HOPG

K

$\Gamma$

NO

NO$^2^+$

+32.0 eV

+22.0 eV

NO$^+$

-3.74 eV

-4.44 eV

cis

trans

(NO)$_2^+$

-8.44 eV

-8.74 eV

cis

trans

 cis

 trans

 cis

 trans

 cis

 trans

 cis

 trans

 cis

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XUV Laser system

Current parameters:

- Wavelength: 50 to 13 (6) nm
- Photon energy: 25 to 95 (206) eV
- Pulse energy: ~ 50 µJ
- Repetition rate: 5 Hz
- Bunches: Single to ~ 30
- Pulse length: 20 to 30 fs

h? = 25 to 206 eV
Third harmonic ~ 600 eV
DESY area in Hamburg

Experimental hall
Experimental set-up

- FEL: 38 eV or 57 eV
- 226 nm or 243 nm
  0.5 mJ/pulse
- 452 nm or 486 nm
  10 mJ/pulse
- 226 nm or 243 nm
  0.5 mJ/pulse
- 1064 nm
  800 mJ/pulse
- 355 nm
  110 mJ/pulse

- atomic hydrogen source
- quartz lens
- SHG
- dye laser
- THG
- C_{60} film
- HOPG
- crystal
- T ~ 100 K
- pulsed NO beam
- TOF
- E_{kin}
- photo diode
- Nd:YAG laser
NO/graphite: double resonance

FEL: 32.0 nm (38 eV)

? t = 3.5 µs
probe delay scan on NO \((v^\text{\prime\prime} = 0, J^\text{\prime\prime} = 11 \frac{1}{2})\):

**FEL:** 32.0 nm (38 eV)

\(T_s = 95\) K
kinetic energy distribution

NO / graphite(0001):
FEL: 32.0 nm (38 eV)

\[ T_{\text{kin}} \approx 1700 \text{ K} \]
\[ T_{\text{kin}} \approx 490 \text{ K} \]

Average energy: \(~ 170 \text{ meV}~\)

For other J\(^{\prime}\)’s: similar distributions
**NO/graphite**

**NO:** adsorbes at $T = 100$ K as $(NO)_2$

Detection via $(1 + 1)$ REMPI at $\lambda \sim 226$ nm

Very sensitive, rotationally and vibrationally state selective

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**FEL:** 21.7 nm (57.1 eV)
Results: NO/HOPG

FEL: 21.7 nm (57.1 eV)

\[ T_{\text{rot}} = 290 \text{ K} \]

\[ T_{\text{rot}} = 690 \text{ K} \]

\[ T_{\text{vib}} = 1600 \text{ K} \]

vibrational population \( \sim 18\% \)
Intensity dependence

FEL: 32.0 nm (38 eV)

\[ Y \sim I^3 \]

similar intensity dependence for FEL at 21.7 nm (57.1 eV) : \[ Y \sim I^{1.4-1.6} \]

non-linear surface photochemistry in the soft x-ray regime
• high rotational excitation: $T_{\text{rot}} \sim 700$ K; $<E_{\text{rot}}> \sim 42$ meV
• high vibrational excitation: $T_{\text{vib}} \sim 1600$ K
  
  gas phase (NO)$_2$ dissociation yields only very low rotational excitation

• NO velocity distribution peaks around 1000 m/s, $<E_{\text{kin}}> \sim 170$ meV

• huge desorption cross section ( $\sim 1 \times 10^{-17}$ cm$^2$)
• **non-linear yield** dependence for NO from (NO)$_2$ / graphite
  
  for both $h? = 38$ and 57 eV

**two – pulse correlation** experiments with the FEL
H atom detection

FEL at 32 nm detected by (2+1) REMPI via the 2s \rightarrow 1s transition at 243 nm

Desorption cross section \sim 1.3 \times 10^{-19} \text{ cm}^2
Hydrogen / graphite

barrierless adsorption for the para position

Hydrogen / graphite

- extremely late arrival times
  - very low kinetic energy of neutral H and D atoms
- low desorption cross section \((1.3 \times 10^{-19} \text{ cm}^2)\) for neutral H
H$^+$ ion detection

FEL induced desorption after dosing with neutral H and D atoms

time-of-flight mass spectrum with kinetic energy resolution

low FEL intensity

FEL at 32 nm
h? = 38 eV
Kinetic energy distribution of $H^+$ directly desorbed from graphite by the FEL pulse.

Average energy: 2.5 eV

$H^+$ yield dependence

FEL at 32 nm $h? = 38$ eV

linear intensity dependence

$? \ \text{DIET process}$
kinetic energy resolving mass spectrum:

**FEL: 32.0 nm (38 eV)**

[Graph showing mass spectrum with peaks labeled H⁺, O⁺, O₂⁺, and NO DR, with a time delay t = 4.0 µs.]
O\(^+\) kinetic energy

FEL at 32 nm (38.7 eV)

average energy: \(~ 1.1\) eV

linear dependence on FEL intensity

DIET process
O$_2^+$ kinetic energy

FEL at 32 nm (38.7 eV)

average energy: ~ 430 meV
NO / graphite

$O_2^+$ desorption from (NO)$_2$ / graphite induced by FLASH

$O_2^+$
FEL: 32.0 nm (38 eV)

$Y \propto I^{10}$

highly non-linear yield
Conclusion

- first laser induced desorption and reaction in the XUV using the Free Electron Laser FLASH

- strong internal excitation of NO: electronic processes

- surprisingly slow neutral H atoms

- fast ions (H\(^+\), D\(^+\), O\(^+\)) with linear yield

- nonlinear yields (NO, O\(_2^+\))

in the future: experiments at low surface temperature with time-correlated FEL pulses
Outlook

- **non-linear yield** dependence for NO from (NO)$_2$ / graphite for both $h\nu = 38$ and 57 eV
- **non-linear yield** dependence for O$_2^+$ from (NO)$_2$ / graphite

**two – pulse correlation** experiments with the FEL

Two – pulse correlator

built together with BESSY for the FEL

ready to be tested at the FEL in a few months