Coherent Control of Surface Reactions using THz Radiation

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• 80% of all important chemical reactions take place on interfaces
• Catalytic processes is the largest chemical industry
• Energy technology, fuel cells, splitting of water by solar
• Environmental science
• Semiconductor technology
• Biosurfaces
Elementary Surface Reactions

desorption  hydrogenation  dissociation  adsorption

soft X-ray Probe

pump

t=t₂

t=t₁

t=0
Challenges for Pump and Probe Experiments

• Most relevant chemical reactions are driven by temperature (kT) not optical excitations
• Synchronization between pump and probe
• Control of reaction coordinate system
• Selective detection of molecules on surfaces, differentiate between species

THz pump and X-ray probe
THz radiation and molecular vibration

1-10 THz = Far-IR (~0.01[eV], ~30[μm]) can excite vibrations: lattice vibration, adsorbate-metal vibration.
**CSR from relativistic e-bunch**

1) wavelength < bunch length ..... incoherent radiation
2) wavelength > bunch length ..... coherent radiation

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<table>
<thead>
<tr>
<th>wavelength [(\mu\text{m})]</th>
<th>1000</th>
<th>100</th>
<th>10</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>energy [eV]</td>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>frequency [THz]</td>
<td>1</td>
<td>10</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

- microwave
- **FIR**
- **IR**
- **VIS-UV**
- **VUV**
- SX

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Ultra short electron bunch is necessary for coherent THz radiation.
Bunch length = **high frequency** cut-off

**HIGH POWER** and **STRONG E-FIELD**
Temperature jump:

vibrational excitation through electron-phonon coupling

Temperature jump via
Electron-hole pair excitation, Lattice vibration excitation,
....
required power: ~1-10 mJ/pulse

fs laser: hot electron problem
THz: NO hot electron

Temperature jump ensues the motion of adsorbate and stimulates surface chemical reactions.
Temperature jump: vibrational excitation

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E-field and surface chemistry

THz electric field ~ Coulomb force between e\(^{-}\) and the nuclei

manipulation of molecule, coherent control molecular motion
How to probe THz induced process

FEL can produce intense X-ray and THz radiation from the same electron bunch.

on-axis radiation, soft X-ray, hard X-ray, off-axis radiation: THz

**Pump:** THz, **Probe:** XPS, XES, XAS, XRD, IR
Summary THz generation

- THz region = far IR $\sim kT$
  - lattice vibration, adsorbate-substrate vibration

- coherent radiation $\sim 10^9 \times$ incoherent radiation
- short electron bunch = high cut-off frequency
- coherent broad band = electric field pulse
- coherent atom manipulation on surfaces

Bunch length: $\sim 100\text{fs}$, Charge: $\sim nC$
Experimental setup

Mass filter

$E$