Fabricating Molecular Nanostructures on Solid Surfaces by Self-Assembly and Nanopatterning

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Diffusing Molecular Adsorbates
Diffusion and Adsorbate Mobility

Due to thermal contact with the surface, at any given temperature the adsorbate can be excited to an energy level that would permit it to jump over the energy barrier. The adsorbate, thus, moves until some other process takes the extra energy away, and the atom stops at a symmetry site different from the starting one.

The series of visited sites are considered as a random walk.

Difusión de Pt/Pt(110) 2×1

T = 61 °C

15×15 nm²

The hopping model

\[ \langle \Delta r^2 \rangle = \left( \Gamma_x \langle \lambda_x \rangle^2 + \Gamma_y \langle \lambda_y \rangle^2 \right) t \]

- Mean Square Displacement
- Hopping frequencies
- Average jump length
The hopping model

\[ D^* = \lim_{t \to \infty} \frac{\langle \Delta r^2 \rangle}{2 dt} \]

Microscopic diffusion coefficient

Dimensionality parameter
(2D = 2, 1D = 1)

IMPORTANT: The microscopic diffusion coefficient is not equal to the macroscopic diffusion coefficient included in Fick’s Law for mass transport.

\[ J = -\mathbf{D} \nabla \rho(\mathbf{r}) \]

Mass flux
Density
Transition State Theory

Hypothesis:
1- ONLY first neighbors jump
2- NO bouncing effects
Transition State Theory

\[ \Gamma = \frac{k_B T}{h} \frac{Z^+}{Z} e^{-E_m/k_B T} = \frac{k_B T}{h} e^{\Delta S^+ / k_B} e^{-E_m / k_B T} \]

For small \( \Delta S (\ll k_B) \), at RT, the prefactor value is about \( 6.3 \times 10^{12} \) s\(^{-1}\).

Another estimation: frustrated translation vibrational mode frequency \( \nu_T \) (about \( 10^{11} \) s\(^{-1}\))

\[ D^* = \frac{1}{2d} \langle \lambda \rangle^2 \nu_T e^{-E_m / k_B T} \]

Arrhenius temperature dependence


4-trans-2-(pyrid-4-yl-vinyl) benzoic acid (PVBA) on Pd(110)
### Tipical Siffusivity Values

<table>
<thead>
<tr>
<th>System</th>
<th>$E_m$ (meV)</th>
<th>$E_d$ (meV)</th>
<th>$D_0$ (cm$^2$ s$^{-1}$)</th>
<th>$\theta$ (ML)</th>
<th>$T$ (K)</th>
<th>Method</th>
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</thead>
<tbody>
<tr>
<td>C/Pt(1 1 1)</td>
<td>1300 ± 200</td>
<td>0.2</td>
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<td>–</td>
<td>860–970</td>
<td>AES</td>
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<tr>
<td>Si/W(1 1 0)</td>
<td>700 ± 70</td>
<td>$3.1 \times 10^{-4} \pm 1.3$</td>
<td>Atom</td>
<td>250–280</td>
<td>FIM</td>
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<tr>
<td>N/W(1 1 0)</td>
<td>900</td>
<td>$1.4 \times 10^{-2}$</td>
<td>–</td>
<td>800–900</td>
<td>AES</td>
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<tr>
<td>N/Fe(0 0 1)</td>
<td>920 ± 40</td>
<td>$8.9 \times 10^{-4}$</td>
<td>Atom</td>
<td>299–325</td>
<td>STM</td>
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<tr>
<td>N/Ru(0 0 0 1)</td>
<td>940 ± 150</td>
<td>$1 \times 10^{-1.7} \pm 1.5$</td>
<td>Atom</td>
<td>300–350</td>
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<tr>
<td>O/Mo(1 1 0)</td>
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<td>$1 \times 10^{-1} \pm 10^{-2}$</td>
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<td>400–600</td>
<td>FEM</td>
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<td>O/W(1 1 0)</td>
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<td>0.4–0.9</td>
<td>1033–1153</td>
<td>CPD$^a$</td>
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<td>610</td>
<td>$2 \times 10^{-7} \pm 1 \times 10^{-4}$</td>
<td>0.15–0.3</td>
<td>500–770</td>
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<td>950</td>
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<td>0.56</td>
<td>500–770</td>
<td>FEM</td>
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<td>1040</td>
<td>0.2/0.4</td>
<td>0.25/0.5</td>
<td>930–1320</td>
<td>SEE$^b$</td>
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<td></td>
<td>1050</td>
<td>$4.5 \times 10^{-4}$</td>
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<td>O/Pt(1 1 1)</td>
<td>$\sim 1200$</td>
<td>$\sim 2.5$</td>
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<td>430 ± 40</td>
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<td>Atom</td>
<td>190–205</td>
<td>STM</td>
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<td>O/Pt(1 0 0)</td>
<td>$\sim 1500$</td>
<td>$\sim 1$</td>
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<td>580–640</td>
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<tr>
<td>O/Pt(1 1 0)</td>
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<td>$2 \times 10^{3} \pm 1$</td>
<td>0–0.2</td>
<td>600–670</td>
<td>PEEM$^e$</td>
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<td>O/Ru(0 0 0 1)</td>
<td>700</td>
<td>${2 \times 10^{-3}}$</td>
<td>Atom</td>
<td>300</td>
<td>STM</td>
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<tr>
<td>O/Al(1 1 1)</td>
<td>1000</td>
<td>${5 \times 10^{-3}}$</td>
<td>&lt;0.1</td>
<td>440</td>
<td>STM</td>
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<tr>
<td>S/Re(0 0 0 1)</td>
<td>790 ± 10</td>
<td>${2 \times 10^{-2}}$</td>
<td>~0.25</td>
<td>300</td>
<td>STM</td>
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<tr>
<td>S/Ni(1 1 1)</td>
<td>290–300</td>
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<td>Atom</td>
<td>105–115</td>
<td>FIM</td>
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<tr>
<td>S/Pt(1 1 1)</td>
<td>570 ± 50</td>
<td>$4 \times 10^{-5}$</td>
<td>Atom</td>
<td>185–200</td>
<td>STM</td>
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<tr>
<td>S/Cu(1 1 1)</td>
<td>250</td>
<td>${1 \times 10^{-4}}$</td>
<td>&lt;0.16</td>
<td>820</td>
<td>QHAS</td>
<td></td>
</tr>
</tbody>
</table>

Model Limits: Long Jumps

Model Limits: Long Jumps

Complex Organic Molecules and Long Jumps

**Decacyclene, DC**

C\textsubscript{36}H\textsubscript{18}

spacers groups ⇒ separation of π-system from substrate

**Hexa-(*tert*-butyl)decacyclene, HtBDC**

C\textsubscript{60}H\textsubscript{66}

50 × 50 Å\textsuperscript{2}
Complex Organic Molecules and Long Jumps

DC/Cu(110)
500 × 500 Å²
T = 194 K
14 s / image

[1 1 0] [0 0 1]
Complex Organic Molecules and Long Jumps

- **DC**
  - Temperature range: 220 - 250 K
  - Activation energy: $E_D = 0.71 \pm 0.05$ eV
  - Pre-exponential factor: $D_0 = 10^{-1.0 \pm 1.0}$ cm$^2$s$^{-1}$

- **HtBDC**
  - Temperature range: 170 - 200 K
  - Activation energy: $E_D = 0.62 \pm 0.04$ eV
  - Pre-exponential factor: $D_0 = 10^{0.9 \pm 1.0}$ cm$^2$s$^{-1}$
Complex Organic Molecules and Long Jumps

\[ \langle (\Delta x)^2 \rangle = \lambda^2 h t \]

Molecular Rotation

Acetylene on Cu(100)

$E_m = 170 \text{ meV}$

Prefactor $= 10^{11.8 \pm 0.2} \text{ s}^{-1}$

Rotation-Translation Coupling

“Lander” Molecules on Cu(110)
Rotation-Translation Coupling

$T = 183\, \text{K}$
$I = -0.23\, \text{nA}$
$V = -1.25\, \text{V}$
$300 \times 300\, \text{Å}^2$

$D = (4.8 \pm 0.5) \times 10^{-17}\, \text{cm}^2/\text{s}$

Rotated molecules
Rotation-Translation Coupling

Diffusion on

Diffusion off
Rotation-Translation Coupling

Lock-and-key effect
Rotation-Translation Coupling

9-thioanthracene on Cu(111)
Atomistic processes in Epitaxial growth

deposition, $F$

aggregation

dissociation, $E_{\text{diss}} = E_b + E_m$

terrace diffusion, $E_m$

edge descent, $E_s$

edge diffusion, $E_e$

nucleation, $i$
Self-Assembly vs. Substrate-Mediated Assembly

The fate of diffusing molecular adsorbates:

1. Finding other adsorbates and creating supramolecular aggregates. When these aggregates are large enough they stop diffusing and are called “islands”. SELF-ASSEMBLY

2. Finding particular sites (surface’s heterogeneity) on the surface, such as defect sites, and attaching to them. NANOPATTERNING
Surface patterns at the nano-scale

- Steps
- Dislocation networks
- Chemically heterogeneous surfaces
Vicinal surfaces and step arrays
Dislocation Networks
How is misfit relaxed in thin metal films?

Simplest case: same in-plane lattice symmetry in film and substrate (only different size)

Perfect Matching

Imperfect Regions:
- Misfit Dislocations

Au(111): Herringbone Reconstruction

6 - 7 nm
Dots nucleated at the elbows of the Au(111) reconstruction

Ni/Au(111)

No need to fine tune the growth temperature!

B. Voigtlander et al, PRB. 44, 10354 (1991)
Self-organized quantum dots

Cobalto/Au(111)

Co islands separated by 2 nm

10 Terabits ($10^{13}/\text{in}^2$)
Effects of Threading Dislocations on Diffusing Adatoms

- Acting directly as nucleation points (unproven)

- Enhanced Exchange for diffusing adatoms which once embedded serve as nucleation spots:
  
  Proposed mechanism for Ni/Au(111)
  
  Enhanced exchange directly observed in 1ML Cu/Ru(0001) and Au(111)


O. Schaff et al., unpublished
PCBM \((C_{72}H_{14}O_2)\)

[6,6]-phenyl C_{61} butyric acid methyl ester

Electron Acceptor
PCBM on Au (111): Functionalizing $C_{60}$ for hcp vs fcc binding site recognition

On Au(111) $C_{60}$ forms close packed structures with weak Van der Waals forces growing from the steps.
PCBM on Au (111) (>0.5 ML):
An organic herringbone or The Nanoscale Spider-Web

Molecular Self assembly dictated by the electronic superlattice of the surface state due to the reconstruction
Extended TTF

Pi-extended TeTrahialFulvane \((\text{C}_{20}\text{H}_{12}\text{S}_4)\)

Electron Donor

\[ \Phi_m \]

LUMO

HOMO
The Organic Donor: ExTTF/Au(111)

Below 1 ML

200 nm x 240 nm

175 nm x 200 nm

exTTF island

clean Au

Electron-Donor exTTF
The Organic Donor: ExTTF/Au(111)

110 nm x 130 nm

23 nm x 26 nm

1 ML
exTTF adsorption geometry
Donor/Acceptor Blends: Segregation at the Nanoscale

Dislocation networks at reconstructed metal surfaces

2 ML Cu/ Ru(0001)
Effect of misfit dislocations on surface diffusion

2 ML Ag/Pt(111) (annealed to 800 K)

Deposition of additional Ag at 110K

Period 7 nm

Ag islands with 62+ 7 atoms

Self-organized growth of Fe dots on the dislocation network of Cu bilayer (13x13) grown on Pt(111)

2 nm Fe dots
Deposited at 60 K and
Annealed at 250 K

3.6 nm separation
10 Terabits/in²

2D “tissue” phase of graphene on Ru(0001)
Ir Clusters on graphene/Ir(111)
Boron Nitride Nanomesh /Rh(111)
Vicinal Au(111) (788)
Mono-disperse Co dots on Au(111) vicinal surface

Self-assembly of colloid particles

Randomly oriented easy axis => more than one particle per bit

Density limit: 1 Tbit/in²

Unprecedented narrow MAE distribution

N. Weiss et al. subm.

Ultra-high density superlattices of Co dots on Au(788)

$\Theta = 0.2$ ML

Best order: $T_{\text{dep}} = 130$ K, $T_{\text{ann}} = 300$ K

Dot lattice coherent over the entire sample surface ($1 \text{ cm}^2$)

Control of the dot size: HWHM = 20%

Unit cell:
mean terrace size = 3.5 nm
dislocation distance = 7.0 nm

Array density: $4 \times 10^{12} \text{ cm}^{-2}$
26 Tdot/in$^2$
0.4 ML Co/Au(788)

Dislocation networks at reconstructed metal surfaces

S. Rousset et al, Univ. Paris
Ordered array of C60 1D nanochains
Chemically heterogeneous surfaces
STM image of a Cu(001) surface after the evaporation of 0.4 ML of atomic nitrogen and subsequent annealing at 600 K for ten minutes. The surface displays a nano-pattern of dark square nitrogen islands (5 nm size) separated by clean bright lines.
Decoration of the Cu grid in c(2x2)N/Cu(100)

\[ \text{c(2x2) 0.4 ML N/Cu(100) \quad 0.1 ML Co / 0.4 ML N / Cu(100) \quad 1.5 ML Co N/Cu(100)} \]

Dots arrays with a density of \(4 \times 10^{12} \text{ cm}^{-2}\) (1000 times more than today)

CuN nanogrid as a pattern for molecular growth

TMP/Cu(100)

20 nm x 16 nm

20 nm x 20 nm

128 nm x 75 nm

42 nm x 79 nm

TMP/N/Cu(100)

25 nm x 25 nm
O/Cu(110) Nanopatterning

- Cu(110) exposed to 1-4 L of O₂ at 625 K ⇒ Alternating 2×1 O/Cu areas with 1D bare Cu areas
- Bare Cu stripes perpendicular to the close-packed [110] direction
- Different adsorption properties: nanopattern for the Lander molecules?
Lander Molecule as a Prototype of Molecular Wire

- Single Lander (C$_{90}$H$_{98}$, SL) molecules consist of an aromatic $\pi$-board and four 3,5 di-tert-butylphenyl groups bonded to the board through rotatable $\sigma$-bonds.

- In gas phase, the phenyl substituents orient perpendicular to the $\pi$-board to avoid the steric hindrance.

- Conducting $\pi$-board + 4 "spacer legs" $\Rightarrow$ Model system for molecular wires on surfaces
Bare Cu Troughs as Preferential Adsorption Sites for SL/O/Cu(110)

- SL rows nucleate exclusively on the bare Cu troughs.
- High degree of lateral order.
The adsorption geometries of the molecules on the troughs are exactly the same as in the bare Cu(110) surface.

The boards of the molecules are perpendicular to the troughs!

Adsorption Geometry of SL Molecules on the Bare Cu Troughs

140 x 140 Å², 0.15 nA, -1.8 V
New Molecular Design: Violet Lander

The adsorption geometry has changed to accommodate the full board of the molecules inside the trough!

Self-assembled Iron Nitride Dots

**standard**
Fe evaporation rate
0.5 ML / min

**slow**
Fe evaporation rate
0.046 ML / min

2000 Å

0.6 ML Fe + N / Cu (100) at 700 K

2.1 ML Fe + N / Cu (100) at 700 K
Self-Organized Iron Nitride Dots

2.3 ML of Fe very slowly deposited in a flux of atomic N (and H) at 700 K

- Island separation: 14 nm
- Island size: 10 nm
- Island height: 0.08 nm
- Island depth: 0.8 nm

5.1 x 10^{11} cm^{-2}
or 3.3 Tb / in^{2}
METHODS to fabricate ARRAYS of SELF-ORGANIZED MAGNETIC DOTS

- Strain Relaxation during Epitaxial Growth
- Ion Sputtering of metal/semiconductor heterostructures
- plus metal Evaporation

- Shadow deposition of Co
Self-Assembly
Intermolecular interactions

- Purely electrostatic (dipolar)
- Dispersive Interactions
- Hydrogen bonding
- Coordination Bonds
Electrostatic Interactions between Adsorbates
Electronically polar molecules

Electronic polarization (e.g., HCl): Atoms with higher electronegativity attract electronic density towards them → Positive and negative charge centers do not coincide → Dipolar moment

\[ p = qr \]

Unit Debye (D) = 3.336 × 10^{-30} \text{ C\cdot m}

Bond’s polarization is determined by atoms electronegativity.

\[ \frac{p}{D} = \chi_A - \chi_B \]

Approx. Additive to bonds

\[ p_{\text{molécula}} \approx \sum p_{\text{enlace}} \]
### Electronically polar molecules

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Dipole moment (Debye units)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkanes</strong></td>
<td>0</td>
</tr>
<tr>
<td>C$_6$H$_6$ (benzene)</td>
<td>0</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
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<tr>
<td>CO</td>
<td>0.11</td>
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<tr>
<td>CHCl$_3$ (chloroform)</td>
<td>1.06</td>
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<tr>
<td>HCl</td>
<td>1.08</td>
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<tr>
<td>NH$_3$</td>
<td>1.47</td>
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<tr>
<td>SO$_2$</td>
<td>1.62</td>
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<td>NaCl</td>
<td>8.5</td>
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<td>CsCl</td>
<td>10.4</td>
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<table>
<thead>
<tr>
<th>Bond moments</th>
<th>Dipole moment (Debye units)</th>
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<td>C—H$^+$</td>
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<tr>
<td>N—H$^+$</td>
<td>1.11</td>
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<tr>
<td>O—H$^+$</td>
<td>1.51</td>
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<tr>
<td>F—H$^+$</td>
<td>1.94</td>
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<tr>
<th>Group moments</th>
<th>Dipole moment (Debye units)</th>
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<tr>
<td>C—OH</td>
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<tr>
<td>C—NH$_2$</td>
<td>1.2 - 1.5</td>
</tr>
</tbody>
</table>

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*a* Data compiled from Wesson (1948), Smyth (1955), Davies (1965) and Landolt-Börnstein (1982).

*b* Depends on conformation (e.g., cyclopropane has a dipole moment).
Zwitterions

From the German “zwiter” = “hybrid”

Molecules provided with acidic and basic groups simultaneously depending on conditions, proton transfer from acidic to basic group.

Example: Glycine

Suggested on surfaces: methionine/Ag(111)

Schiffrin et al. PNAS 104, 5281 (2007)
Dipolar interactions

Ion-dipole interaction

\[ U(r, \theta) = -\frac{ze \cdot p \cos \theta}{4\pi\varepsilon_0 r^2} \]

For a Na\(^+\) ion and a water molecule in close contact (\(r = \text{radius(Na}^+\)+radius(agua) = 2.35 Å), the interaction energy would be about 1 eV, i.e. 39\(k_B\)T at RT

Dipole-dipole interacción

\[ U(r, \theta_1, \theta_2, \phi) = -\frac{p_1p_2}{4\pi\varepsilon\varepsilon_0 r^3} \left[ \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi \right] \]

The interaction energy for two molecules with dipole moment 1D separated 3.6 Å, maximum interaction is just about \(k_B\)T at RT
Molecular polarizability

Subject to a external applied electric field, negative and positive charge centers split → induced dipole moment $\mathbf{p}_{\text{ind}}$.

$$\mathbf{p}_{\text{ind}} = \alpha \mathbf{E}$$

Units $4\pi\varepsilon_0 \times \text{(volume)}$ or $\text{C}^2\text{m}^2\text{J}^{-1}$

Approx. additive towards bond polarizabilities (or towards group polarizabilities for delocalized electron systems)

<table>
<thead>
<tr>
<th>Atoms and molecules</th>
<th>$\alpha$</th>
<th>Atoms and molecules</th>
<th>$\alpha$</th>
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<tbody>
<tr>
<td>He</td>
<td>0.20</td>
<td>NH$_3$</td>
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<td>H$_2$</td>
<td>0.81</td>
<td>CH$_4$</td>
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<td>H$_2$O</td>
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<td>HCl</td>
<td>2.6</td>
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<td>CO$_2$</td>
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<td>Ar</td>
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<td>CH$_3$OH</td>
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<td>CO</td>
<td>1.95</td>
<td>Xe</td>
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<table>
<thead>
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<th>Bond polarizabilities</th>
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<th>Bond polarizabilities</th>
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<td>Aliphatic</td>
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<td>C—C</td>
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<td>C—O</td>
<td>0.60</td>
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<tr>
<td>C=C</td>
<td>1.07</td>
<td>C=O</td>
<td>1.36</td>
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<tr>
<td>C=O</td>
<td>1.65</td>
<td>N—H</td>
<td>0.74</td>
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<td>C−H</td>
<td>0.65</td>
<td>C−Cl</td>
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<tr>
<td>O−H</td>
<td>0.73</td>
<td>C−Br</td>
<td>3.75</td>
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Molecular groups

<table>
<thead>
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<th>$\alpha$</th>
<th>Molecular groups</th>
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<tbody>
<tr>
<td>C—O—H</td>
<td>1.28</td>
<td>CH$_2$</td>
<td>1.84</td>
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<tr>
<td>C—O—C</td>
<td>1.13</td>
<td>Si—O—Si</td>
<td>1.39</td>
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<tr>
<td>C—NH$_2$</td>
<td>2.03</td>
<td>Si—OH</td>
<td>1.60</td>
</tr>
</tbody>
</table>

* Polarizabilities $\alpha$, are given in units of $(4\pi\varepsilon_0)^{-1} = (4\pi\varepsilon_0) \frac{10^{-10} \text{m}^3}{1.11 \times 10^{-10} \text{C}^2 \text{m}^{-1} \text{J}^{-1}}$. Note that when molecules are dissolved in a solvent medium their polarizability can change by up to 10%. Data compiled from Denbigh (1940), Hirschfelder et al. (1954) and Smyth (1955).
Metallic surfaces

- Jellium model: positive charge distribution is assumed to be homogeneous.
- Electronic density smoothes out positive-charge density contours.
- Not all the electronic wavelengths allowed, limited by Fermi wavelength → Friedel oscillations.

Zangwill, Physics at Surfaces, Cambridge University Press (1990)
Screening by surface state electrons

200 nm  V=1.2 mV, i=1.5 nA  Cu(111)  50 K
How to avoid screening

Porphyrin

Yokoyama et al. Nature 413, 619 (2001)
How to avoid screening
Cyanophenyl-cyanophenyl interaction

\[ p = 3.32 \text{ D} \]

0.31 eV

0.55 eV

a

b
Dipolar supramolecular aggregates

Yokoyama et al. Nature 413, 619 (2001)
STABILIZATION OF SUPERLATTICES BY FRIEDEL OSCILLATIONS IN SURFACE STATES

Cu/Cu(111)  Ce/Ag(111)

F. Silly et al PRL 92, 016101 (04)

(θ = 8 × 10^{-3} ML, T = 3.9 K, V_t = 0.1 V and I_t = 10 pA).
vdW Interactions between Adsorbates
London dispersion forces

- For any atom $\langle p(t) \rangle = 0$, but $p(t) \neq 0$
- Instantaneous electric field
- Polarization of neighboring atoms
- London force = attraction force between instantaneous dipole and induced dipole.
- In vacuum, London dispersion forces are always attractive.
- Non-directional
Estimation

• Bohr radius

\[ a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} = \frac{e^2}{2(4\pi \varepsilon_0) h} = \frac{e^2}{2(4\pi \varepsilon_0) l} \]

• Instantaneous dipole at atom 1 \( p_1 = ea_0 \)

• Field created by atom 1’s dipole at atom 2 position

\[ E(r, \theta) = p_1 \sqrt{1 + 3 \cos^2 \theta} / 4\pi \varepsilon_0 r^3 \]

• Induced dipole on atom 2 (polarizability \( \alpha \)) \( p_2 = \alpha E \)

• Interaction energy between \( p_1 \) and \( p_2 = (1/2)p_2E \)

\[ U(r, \theta) = \frac{\alpha e^6}{8(4\pi \varepsilon_0)^4 \hbar^2 \nu^2 r^6} \left(1 + 3 \cos^2 \theta\right) \]
Estimation

- As time goes by, instantaneous dipole $p_1$ changes in a random manner, and thus changes $\theta$. The time-average of the angle dependent factor for the energy is $\langle 1 + \cos^2 \theta \rangle = 2$

- Bohr’s atom polarizability $\alpha = 4\pi a_0^3$

$$\langle U(r) \rangle \approx -2\alpha_0^2\hbar \Omega / 4\pi \varepsilon_0 r^6$$

But for a numeric factor, this estimation agrees with the one calculated by London in the 1930’s using quantum-mechanical perturbation theory.

$$U(r) = - C_{disp} / r^6 = - \frac{3}{4} \frac{\alpha_0^2\hbar \Omega}{4\pi \varepsilon_0 r^6}$$
Properties

• Non-directional
• Always attractive (please, note, only in vacuum)
• Almost additive (especially in vacuum)
• Order of magnitude: for $a_0/4\pi\varepsilon_0 \sim 1.5 \times 10^{-30} \text{ m}^3$
  and $h\nu = 12.5 \text{ eV}$, $U \sim k_B T$
• Dispersion interaction always exists, even for molecules with no particular functional groups. THUS IT IS THE MAIN SOURCE FOR INTERACTION IN MOLECULES WITH NO POLAR OR REACTIVE GROUPS.
Steric or Pauli repulsion

Close contact between two neighboring atoms or molecules → onset of Pauli repulsion

Not well defined functional form

Hard-Sphere model

\[ U(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} = \frac{\kappa}{r} \quad n \to \infty \]

Inverse power model

\[ U(r) = \frac{\kappa}{r^n} \]

Exponential model

\[ U(r) = ce^{-r/\sigma} \quad c > 0 \]
Van der Waals Interaction

Attractive part: dispersion forces.
Repulsive part: steric repulsion
Lennard-Jones potential

\[ U(r) = A/r^{12} - B/r^6 = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]
VdW Radii

- Typical values 1 - 2 Å
- It is about 0.8 Å smaller than the covalent radius
VdW and close-packing

vdW interaction effects

1. It brings the molecules as close as is possible provided that not two atoms get closer than the sum of their vdw radii.

2. It thus tends to align molecules with non-spherical symmetry.

3. It makes complementary-shaped pairs of molecules to bind so the shapes fit to each other.
C60/Au(111)
Chiral Close-packing of Achiral-Species

TMP (meso-tetramesitylporphyrin)

TMP/Cu(100) at low coverage and at low T

226 nm x 235 nm

20 nm x 16 nm
Chiral Close-packing of Achiral-Species

- HOMO-2: -6.3 eV
- HOMO-1: -4.9 eV
- HOMO: -3.4 eV
- LUMO: 2.8 eV
Chiral Close-packing of Achiral-Species

114 × 130 nm²

10 × 13 nm²
Chiral Close-packing of Achiral-Species

34 × 35 nm²

D. Écija et al. In prep.
Organizational and Adsorption-Induced Chirality in HtB-HBC/Cu(110)

Adsorption Induced chirality: + or -5° rotation
Organizational chirality: L or R close-packing

All the molecules with +(-) rotation assemble only into the R(L) geometry

Hydrogen-bonded networks
Hydrogen-bonding

- X and A are electronegative species (typically O, N, F, etc...)
- X-H donor; A acceptor
- Typical energies of 0.1 eV per bond, but can be as high as 2 eV
The nature of hydrogen-bonding

Complex interaction:

1. Electrostatic (donor and acceptor groups show dipolar moments \(-\delta^--\delta^+-\)

2. Polarization

3. Charge transfer

4. London’s dispersive interaction

5. Steric repulsion

Hydrogen-bonding classification

<table>
<thead>
<tr>
<th></th>
<th>Strong</th>
<th>Moderate</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>interaction type</td>
<td>strongly covalent</td>
<td>mostly electrostatic</td>
<td>electrostat./ dispers.</td>
</tr>
<tr>
<td>bond lengths [Å]</td>
<td>1.2–1.5</td>
<td>1.5–2.2</td>
<td>&gt; 2.2</td>
</tr>
<tr>
<td>H⋯A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lengthening of X–H [Å]</td>
<td>0.08–0.25</td>
<td>0.02–0.08</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>X–H versus H⋯A</td>
<td>X–H ≈ H⋯A</td>
<td>X–H &lt; H⋯A</td>
<td>X–H ≪ H⋯A</td>
</tr>
<tr>
<td>X⋯A [Å]</td>
<td>2.2–2.5</td>
<td>2.5–3.2</td>
<td>&gt; 3.2</td>
</tr>
<tr>
<td>directionality</td>
<td>strong</td>
<td>moderate</td>
<td>weak</td>
</tr>
<tr>
<td>bond angles [°]</td>
<td>170–180</td>
<td>&gt; 130</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>bond energy [kcal mol⁻¹]</td>
<td>15–40</td>
<td>4–15</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>relat. IR shift Δνₓₜₜ [cm⁻¹]</td>
<td>25 %</td>
<td>10–25 %</td>
<td>&lt; 10 %</td>
</tr>
<tr>
<td>¹H downfield shift</td>
<td>14–22</td>
<td>&lt; 14</td>
<td></td>
</tr>
</tbody>
</table>

1 kcal/mol ≈ 43.4 meV

Where’s the hydrogen??

Bonding directionality

Donor group directionality

Bonding directionality

Acceptor group directionality along the lone pairs
Non-additivity: $\sigma$-cooperativity

- Hydrogen-bond formation modifies significantly donor and acceptor properties: non-additivity.
- Hydrogen bond formation $-X^\delta-\cdots H^\delta+ ---- A^\delta-$ makes de group $-X^\delta-\cdots H^\delta+-$ even more polar.
- If $X^\delta-$ also plays the acceptor role for another hydrogen-bond $-Y^\delta-\cdots H^\delta+ ---- -X^\delta-\cdots H^\delta+-$, then formation of the bond $-X^\delta-\cdots H^\delta+ ---- A^\delta-$ strengthens the bond $-Y^\delta-\cdots H^\delta+ ---- -X^\delta-\cdots H^\delta+$

Non-Additivity: $\pi$ cooperativity

Resonance-Assisted Hydrogen Bonding (RAHB)

Making an H-bond helps stabilizing the zwitterionic, i.e. it shifts equilibrium towards the right-hand side.

Zwitterionic canonical form more polar than neutral form $\rightarrow$ strengthening new bonds
Open, random networks of cytosine on Au(111)

R. Otero et al. Science
319, 312 (2008)
Guanine self-assembly on Au(111)

The unit cell is a supramolecular aggregate consisting of four molecules.

Calculated STM image for a planar adsorption geometry

Mirror-symmetric image
Guanine quartets
The high-temperature phase

Annealed to 120°C

G-quartet is not the most stable structure. Why is it the only one appearing when you deposit at RT?
Non-Additivity

DFT calculations
Hydrogen-bonded dimer formation leads to an intramolecular charge redistribution...

... which increases quartets binding energy.
RT stability of the different supramolecular aggregates

Assuming an attempt frequency of $10^{-14} \text{ s}^{-1}$

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Formation Energy (eV)</th>
<th>Stability at RT (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer</td>
<td>0.44 eV</td>
<td>$2 \times 10^{-7}$</td>
</tr>
<tr>
<td>Trimer</td>
<td>1.24 eV</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Quartet (No RAHB)</td>
<td>1.76 eV</td>
<td>5</td>
</tr>
<tr>
<td>Quartet (RAHB)</td>
<td>3.36 eV</td>
<td>$10^{14}$</td>
</tr>
</tbody>
</table>
PCBM on Au (111): Functionalizing C60 for hcp vs fcc binding site recognition

On Au(111) C₆₀ forms close packed structures with weak Van der Waals forces growing from the steps.
PCBM on Au (111): Functionalizing C60 for hcp vs fcc binding site recognition

(<0.1 ML)
PCBM on Au (111) (>0.5 ML) : An organic herringbone or The Nanoscale Spider-Web

What if you deposit an electron donor on top of this?

Nano Lett. **2007**, 7, 2602
The Spider-Web with Molecular Resolution

Molecular double chains on fcc domains

23.5 x 26.4 nm²

1000Å
Site-Selective Adsorption and the Organic Addend

- Organic addend “touching” the surface.
- Organic addend avoids DW areas + vdw attraction between the C60 heads = SITE SELECTIVITY

HCP DW FCC DW HCP

HCP DW FCC DW
Crossover from Site-Selective to Site-Independent Adsorption
Weak H-Bonds Help Stabilizing the High-Coverage Structure

• DFT calculations: See Wang’s talk later in this session

• Freestanding ML: no role of the substrate BUT...

... Good agreement with experimental results...

... ????????
Collective effect of intermolecular interactions on adsorption geometry

- Organic addend involved in H-bonding and not “touching” the surface → site-independent adsorption.
- Intermolecular Interactions modify adsorption geometry and substrate-molecule interactions leading to the removal of site-selectivity

Coordination bonds with metal atoms
Lewis acids and bases

**Lewis base**: any compound with a lone pair

**Lewis acid**: any compound with an empty orbital

$\text{Mg}^{+2}$ (3s empty), $\text{Ag}^+$ (1 orbital 5d empty), $\text{Al}^+$ (1 orbital 3p empty)

**Coordinate covalent bond**: covalent bonding between two atoms or compounds in which both electrons shared in the bond come from the same atom.
Coordination compound: it is the result of an acid/base Lewis reaction in which a coordinate covalent bond is formed between a neutral or anionic molecule and a metallic cation.

Organometallic compound: coordination compound in which carbon-metal bonds are formed.
σ donation

The interaction between occupied σ orbitals (lone pair) and d orbitals of the metal with the right symmetry lead to an attractive interaction.

The interaction of antibonding $\pi$ orbitals with filled d metal orbitals leads to an attractive interaction.
Why is CO such a common ligand?
Are we alone?

TMA/Cu(100) deposited at RT and studied between 250 K y 300 K

Codepositing metals and organic species

Deposition at 100 K
Codepositing Metals and Organic Species

Hierarchy in coordination-bond mediated molecular self-assembly

Codepositing Metals and Organic Species

Deprotonation of carboxylic group into carboxylate
