Chirality: New Surface Science Insights on a 160-year old subject

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University of Liverpool, UK
REVIEW LITERATURE:

S.M. Barlow and R. Raval,
Complex Organic Molecules at Metal Surfaces: Bonding, Organisation and Chirality.
Surface Science Reports, 50 (2003) 201-341

R. Raval
Assembling Molecular Guidance Systems for Heterogeneous Enantioselective Catalysis.
CATTECH, 5 (2001) 12-28

V. Humblot, S.M. Barlow and R. Raval,
Two-Dimensional Organisational Chirality through Supramolecular Assembly of Molecules at Metal Surfaces.

S.M. Barlow and R. Raval,
Nanoscale insights in the creation and transfer of chirality in amino acid monolayers at defined metal surfaces

R. Raval,
Chiral Expression at Metal Surfaces: Insights from Surface Science Techniques.
Chemical Society Reviews, 2009 (38) 707-721.
Optical Activity (Jean-Baptist Biot 1815)
Rotation of plane polarised light

Tartaric Acid Salt Crystals (Pasteur 1848)
contain no inversion symmetry elements
i.e. No mirror planes, improper rotation axes, inversion centres
MIRROR FORMS CANNOT BE SUPERIMPOSED
BY TRANSLATION OR ROTATION

A geometrical property with profound implications for

PHYSICS  CHEMISTRY  BIOLOGY
• The tetrahedral carbon  
  Van’t Hoff & Le Bel 1874.

• Stereochemistry/
  Molecular chirality  
  Fischer 1894/ Prelog 1975

Optical isomers enantiomers chiral molecules
Chiral Nomenclature

1) By Optical Activity

- Levorotatory: \( \alpha(-) \)
- D- and L- enantiomers

2) By Configurations D- and L- relating the molecule to glyceraldehyde

D- and L- are NOT related to optical activity (+/- or d/l)

3) Cahn Ingold Prelog rules:
Substituents at chiral centres given a priority, based on atomic number.
Hold molecule so lowest priority substituent is held away.
Connect remaining group from lowest to highest.

Clockwise Rectus
Labelled R

Anti-Clockwise
Sinister
Labelled S
Point chirality at a single *stereogenic centre*

Chirality arising from steric factors

Chirality arising from organisation in 3D
Properties of enantiomers

Normally, the two enantiomers of a molecule behave identically to each other i.e. Have same physical properties e.g. melting point, density.

However, they behave differently in chiral environment:

Different interaction with right- and left-circularly polarised light

Different interaction with chiral environment
HOMOCHIRALITY OF LIFE ON EARTH

From NASA
http://visibleearth.nasa.gov
Different Physiological Effects of Enantiomers

- **S-limonen**: Harsh, turpentine, hint of lemon
- **R-limonen**: fresh citrus, odor of orange
- **L-carvone**: smells of spearmint
- **D-carvone**: Smells of caraway
Different Physiological Effects of Enantiomers

- **D-thalidomide:** relieved morning sickness in pregnancy
- **L-thalidomide:** mutagenic agent, teratogen
- **S-penicillamine:** antiarthritic drug
- **R-penicillamine:** highly toxic
- **S-propanolol:** beta-blocker (heart disease)
- **R-propanolol:** active contraceptive
Pharmaceuticals, fragrances, agrochemicals, etc must select correct chirality to deliver correct function.

The Ultimate in Molecular Recognition!!!
Pharmaceuticals, fragrances, agrochemicals, etc must select correct chirality to deliver correct function.

Two approaches:
Asymmetric Synthesis

Current technologies:
* Organic synthesis/
* Homogeneous catalysis

Chiral separation

* Crystallisation
* Chromatography
Chirality at Surfaces: towards important Technologies

• Heterogeneous enantioselective catalysis
• Pharmaceuticals (chiral separations)
• Non-linear Optical Devices
• Biosensors
• Smart Coatings
Creating Chiral Solids

- Chirally modified solid surfaces
- Intrinsically chiral solid or surfaces

- Chiral modifier
- 'Bare' or as support for active centres

Raval
CATTECH, 5 (2001) 12-28
Surfaces: Congregators of Molecules and Breakers of Mirror Symmetry

Chiral Surfaces

Mirror symmetry-breaking processes at Surfaces?
Chirality via Adsorption of Molecular Systems

chiral centres of molecule preserved

Retaining Point Chirality of Molecular System

Retaining Chiral Organisation of Molecular System
Surface Induced Chirality

Adsorption-Induced Chiral Motif

Adsorption-Induced Organisation
Point Chirality
R. Raval, Chemical Society Reviews, 2009 (38) 707-721.
Point Chirality

3-Dimensions
- 32 crystallographic point groups

2-Dimensions
- 10 crystallographic point groups

Chiral 2-Dimensions
- 5 chiral point groups

Only one allowed: Globally chiral system

Mirror motifs

Both allowed: Overall racemic system
Organisational Chirality
Organisational Chirality

230 space groups

17 space groups

5 chiral space groups

Only one Mirror unit
Mesh allowed

R. Raval,
Chemical Society Reviews, 2009 (38) 707-721.
Both chiral unit meshes allowed
Assembling Chiral Entities

Racemic Conglomerate
Homochiral Unit cell

Racemic Compound
Heterochiral Unit Cell
So which one forms?
• Depends on conditions (e.g. T)
• Depends on Dimensions

Conglomerate: Compound

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Racemic</th>
<th>Homochiral</th>
<th>Heterochiral</th>
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<tbody>
<tr>
<td>3D</td>
<td>10</td>
<td>:</td>
<td>90</td>
</tr>
<tr>
<td>2D</td>
<td>70</td>
<td>:</td>
<td>30</td>
</tr>
</tbody>
</table>
Transmission of Chirality

Tartaric Acid Salt Crystals (Pasteur 1848)

levorotatory 
1-enantiomer

COOH
H
HO
H
COOH

R,R, Tartaric Acid

dextrorotatory 
d-enantiomer

COOH
HO
H
H
COOH

S,S, Tartaric Acid

Transmission of Chiral Information

10^{-2} \text{ m}

10^{-10} \text{ m}
Transmission of Chirality Mapped at the Nanoscale

Rubrene/Au(110) driven by Molecule-Molecule Interactions

Transmission of Chirality at Surfaces

Tartaric Acid on Cu(110) driven by Molecule-Surface Interactions

R,R, Tartaric Acid
Defined Cu(110) surface

Molecular information & Orientation

Chemical composition of surface

Geometry & 2-Dimensional order

RAIRS

IR

v=0

v=1

v=2

XPS

DFT

LEED

STM

X-Ray

e⁻

Tunnelling current

low energy

e⁻
Complex Surfaces need Complementary Techniques

Chemical information

Spatial resolution

RAIRS

XPS

LEED

STM

DFT Theory
Transmission of Chirality at Surfaces

Tartaric Acid on Cu(110) driven by Molecule-Surface Interactions

R,R, Tartaric Acid
Adsorption Phase Diagram for R,R-Tartaric Acid on Cu(110): Dynamical changes in local chiral motif. Chiral and Achiral Organisations.

b) Adsorption phase diagram for R,R-Tartaric acid on Cu(110)

- **405 K**: bitartrate (90°) → high coverage monotertrate monolayer (41°)
- **350 K**: mono-tertrate (40°) → bitartrate (90°) → slow change with time
- **300 K**: low coverage monotertrate monolayer → Dimers and monomers
- **83 K**: weakly perturbed neutral bi-acid molecules (HOOC - CHO - CHO - COOH) → bi-acid multilayer

Increasing coverage
Polymorphism of Local Motifs and of Aggregates

- One chiral molecule
- Different chemical forms
  - Different bonding/orientation forms
  - Variations in 2-D arrangements

Many surface phases
Enantiopure (R,R)-TA on Cu(110)
Perfect Point Group and Space Group Chirality

Ortega, Muryn, Baddeley and Raval,
Nature 404(2000)376;
Perfect Point Group and Space Group Chirality

DFT-Sautet
JACS 2001 (123) 6639

10 x 10 nm²

Nanosized Channel
R,R-tartaric acid: Adsorption Induced Stress (through metal)

Cu-Cu from 2.58Å to 2.62Å upon adsorption

+5 kJ.mol$^{-1}$

More than 3 in a row & no 2 empty `Cu sites in between
Is there chirality transfer from Single adsorbates to the Organised Structure?

S,S, Tartaric Acid

R,R, Tartaric Acid
Chirality transfer from single adsorbates to the aggregate.

R,R-tartaric acid

Ortega, Muryn, Baddeley and Raval, Nature 404(2000)376
HIERARCHIES OF CHIRALITY

(R,R)-tartaric acid/Cu(110)  (S,S)-tartaric acid/Cu(110)

a) Level 1
Preservation of Chiral centres upon Adsorption

b) Level 2
Adsorption induced chiral distortion of molecular backbone

c) Level 3
Organisation of adsorbates into chiral arrangement that break mirror symmetry of Cu(110)

d) Level 4
Adsorption stress leads to creation of vacant, chiral nanochannels

Vacant, chiral nanochannel
Modelling Chiral Packing

Barbosa, Sautet  J. Am. Chem. Soc. 2001 (123) 6639

Molecule under the surface structure in Gas-phase

packing

Molecules under the (3 1,1 2) array in Gas-phase

distortion

interaction

Molecules under the (3 1,1 2) array on surface
Energy Diagram of the molecular adsorption

Barbosa, Sautet J. Am. Chem. Soc. 2001 (123)6639

(1) R,R-isomer
(2) S,S-isomer (optimized)
(3) R,R-mirror

Deformation energy

Deformation + packing

Interaction energy (similar ~165 kJ.mol⁻¹)

Adsorption energy

Reorganization of H bonds
Local Adsorption Motif Dictates Enantiomorphous Separation

**R,R-isomer**

- Local mirror

**S,S-isomer**

- Lateral interactions

**Optimized position**

- 2.04 Å : 10 kJ mol⁻¹

Relief of H-H interaction disturbs intramolecular H bonds

Barbosa, Sautet, JACS, 2001 (123) 6639
Racemic Mixture: 2-D chiral resolution into enantiomorphous conglomerates

Separate areas with structure of \((S,S)\)- and \((R,R)\)-TA

Racemic Mixture

Haq, Liu, Humblot, Jansen and Raval, Nature Chemistry 2009 (1) 409-414

NB: Conglomerate formation seems more favoured in 2D.
CHIRALITY FROM NON-CHIRAL UNITS?

Can adsorption create chirality?
CHIRALITY FROM NON-CHIRAL UNITS?
Achiral Molecules on Achiral Surfaces.

R,R-tartaric acid

Succinic acid

V. Humblot, M. Ortega Lorenzo, C. Baddeley, S. Haq, R. Raval
High coverage Achiral Assembly

80Å x 80Å
High coverage Heterochiral Structure

Liu, Haq, Darling, Raval
Angew. Chem. 47 (2007) 7613

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80Å x 80Å

p(4x2)

45 eV
Chiral Recognition by racemic assembly?

Can we get Chiral Recognition of Guest Molecules?

S,S, Tartaric Acid

R,R, Tartaric Acid
Two chiral forms of SU: 
(R, R)-TA: 🔴 (S, S)-TA: 🔵

Fig. 3
Single-site : Single-molecule Chiral Recognition

Liu, Haq, Darling, Raval
Angew. Chem. 47 (2007) 7613
Amino-Acids at Metal Surfaces:
Can we take our Analysis to the Single-Molecule Level?

Proline
-Unique amino acid- NH group is contained within a pyrrolidine ring

Forster, Dyer, Persson, Raval, JACS. 2009, 131, 10173-10181
Proline at Cu(110) Surface

Prolate
Enantiopure (S)-Proline on Cu(110) – The (4 2) phase
Bonding and Adsorption Footprints

<table>
<thead>
<tr>
<th>Structure</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tr>
<td>$E_{ads}$ (eV/molecule)</td>
<td>1.23</td>
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Forster, Dyer, Persson, Raval, JACS. 2009, 131, 10173–10181
Bonding and Adsorption Footprints

2 mirror chiral footprints Adopted

How are they organised??
# Energetics of Eight Overlayer Arrangements Computed

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Simulating STM Images
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(S)-Proline/Cu(110) – Molecule-by-Molecule Analysis

Calculated

Experimental
Adsorption FootPrints and Conformations—Molecule-by-Molecule Analysis
(S)-Proline/Cu(110) – Molecule-by-Molecule Analysis

Forster, Dyer, Persson, Raval, JACS. 2009, 131, 10173–10181
1D H-Bonded chains along [1-10]
Detecting Individual Molecular Chirality

- Conformer A
  - R
  - S

- Conformer B
  - R
  - S
From Enantiopure To Racemic Systems
Racemic Proline on Cu(110)

Forster, Dyer, Persson, Raval, Angewandte Chemie, 2010, DOI: 10.1002/anie.200904979
Detecting Individual Molecular Chirality And Individual Footprints
Molecular Chirality vs Footprint Chirality

Molecular Chirality scrambled

Strict Footprint Chirality
CHIRALITY AT SURFACES

UNDERSTANDING TRANSMISSION OF CHIRALITY FROM NANO to MACROSCALE

SURFACES AS ORGANISERS AND SEGREGATORS OF CHIRALITY

SURFACES AS CREATORS OF CHIRALITY

CHIRAL FOOTPRINTS
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