Surface Science 613 (2013) 1–5

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Surface Science Prospectives

Molecular chirality in surface science

Karl-Heinz Ernst *

Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
Organic Chemistry Institute, University Zurich, CH-8057 Zürich, Switzerland

ARTICLE INFO

Article history:
Received 12 January 2013
Accepted 14 March 2013
Available online 26 March 2013

Keywords:
Chirality
STM
Organic molecules
Single crystals

ABSTRACT

The adsorption of ever-larger organic molecules onto well-defined solid surfaces has been pursued during the last decade of surface science. One important consequence of adsorbing large molecules is a mismatch of molecular size and surface lattice, which leads frequently to mirror symmetry breaking and establishes handedness to the adsorbate complex, even if the molecule itself is not chiral. In addition, adsorption of chiral molecules, i.e., those lacking mirror symmetry before adsorption, has been performed increasingly. Such studies are not limited to the liquid–solid interface, but also cover the UHV domain. The principles of mirror symmetry breaking due to molecular adsorption are reviewed and ramifications of chiral bias in molecular layers are discussed.

1. Introduction

In 1848 Louis Pasteur separated manually crystals, distinguishable by opposite handedness in their shape, which were obtained from a tartaric acid salt solution. The aqueous solutions of the two crystal batches showed then opposite rotation of plane-polarized light, actually the only physical effect addressing molecular structure in the 19th century. Pasteur made the connection of the lack of mirror symmetry in crystals (*enantiomorphism*) to the handedness of molecules building such crystal already at a time when chemists had little conception about molecular structure and physicists were far from being ready to accept the existence of atoms [1]. His vague speculations about the reason for left- or right-handedness in molecules sparked the development of stereochemistry [2], which concerns the absolute or relative positions of atoms in space in a molecule. Over the last 150 years, the concept of chirality has strongly promoted organic and inorganic stereochemistry [3,4]. Two puzzling aspects of Pasteur's experiment are worth to be discussed: 1) The left- and right-handed molecules (*enantiomers*) did not form a mixture of both (called a *racemate*) in a single crystal [5], but rather became separated in form of a *conglomerate* of homochiral crystals. Hence, each single crystal contained only molecules of one mirror kind. Why this happens only for some compounds and under which conditions is still not understood today. 2) The broken-mirror-symmetry aspect of molecular structure was transferred to the macroscopic shape of the tartrate crystals. In β-quartz, for example, SiO_4 tetrahedrons are aligned in a helical fashion, however, no computational method whatsoever is able to predict from this information the macroscopic shape of the crystal, including the asymmetric expression of {511} faces (Fig. 1a). It is difficult to address these problems directly, and meaningful model systems are needed. This applies also to *enantioselective* heterogeneous catalysis, which is concerned with synthesis of chiral molecules of single handedness at a surface (Fig. 1b) [6,7]. Chirality plays also a role in molecular motors, rotors and switches at surfaces, a highly topical issue in nanotechnology [8]. Another motivation for studying chiral molecules at surfaces comes from understanding biomineralization. Chiral molecules – basically proteins and polysaccharides – interact with achiral mineral surfaces during crystal growth and give single crystals or composite materials a sophisticated chiral shape [9]. Proteins with substantial aspartic acid and glutamic acid content, for example, have been extracted from calcite, aragonite and hydroxyapatite biominerals [10–12]. Because these acidic proteins are homochiral, they induce chirality into otherwise achiral minerals, and the macroscopic crystals show chirality. As example stands calcium oxalate, whose crystals extracted from tomato and tobacco leaves show chiral pseudo-tetrahedral shape [13].

Chirality arrived to ultrahigh vacuum (UHV) surface science in 1978 when Somorjai et al. studied chiral and achiral amino acids on copper surfaces [14]. After scattered studies at the liquid–hopg interface [15,16], chiral UHV surface science took off at the end of the last century [17–21]. Since then, many new phenomena about chirality at surfaces have been described and were covered by topical reviews [22–28]. This prospective briefly introduces basic principles of chirality at surfaces, including mirror-symmetry breaking upon adsorption and transfer of handedness from the single chiral molecule into two-dimensional (2D) crystals. It discusses relatively new phenomena, like chiral surface reconstructions and cooperative effects leading to symmetry breaking in entire layers due to chiral bias and gives an outlook for the next decade.

---

* Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland. Tel.: +41 58 765 43 63; fax: +41 58 765 4034.
E-mail address: elgarah@emt.inrs.ca.

0039-6028/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.susc.2013.03.014

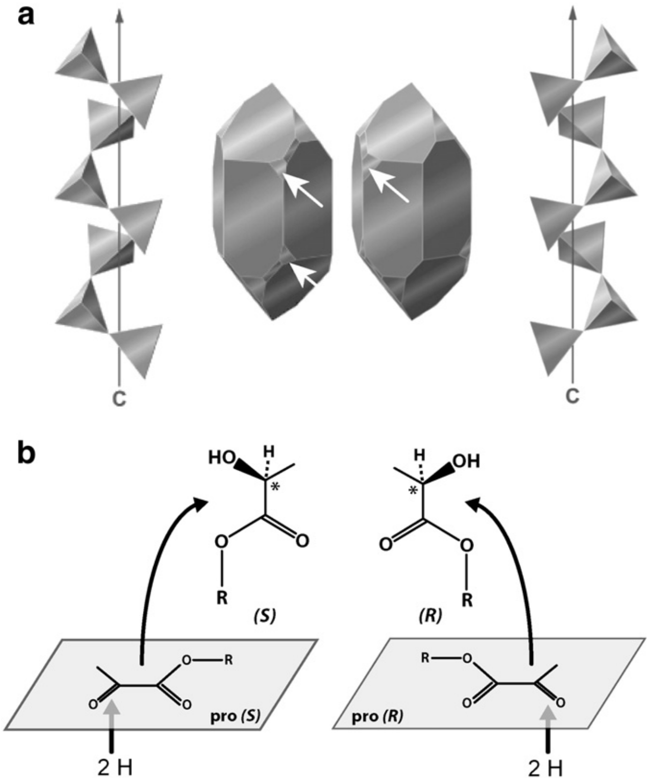

Fig. 1. (a) Principle of enantiomorphism in crystals. β-quartz crystals show {511} facets such that they lack mirror symmetry. The macroscopic handedness correlates with the sense of the helical alignment of SiO_4 tetrahedrons. (b) Sketch for enantiospecific hydrogenation of pyruvic acid ester to lactic acid ester over platinum. A coadsorbed chiral modifier (not shown) steers prochiral reactants into one of the two shown enantiomorphous adsorbate alignments. A directed attack of the hydrogen from one side will then create only one enantiomer.

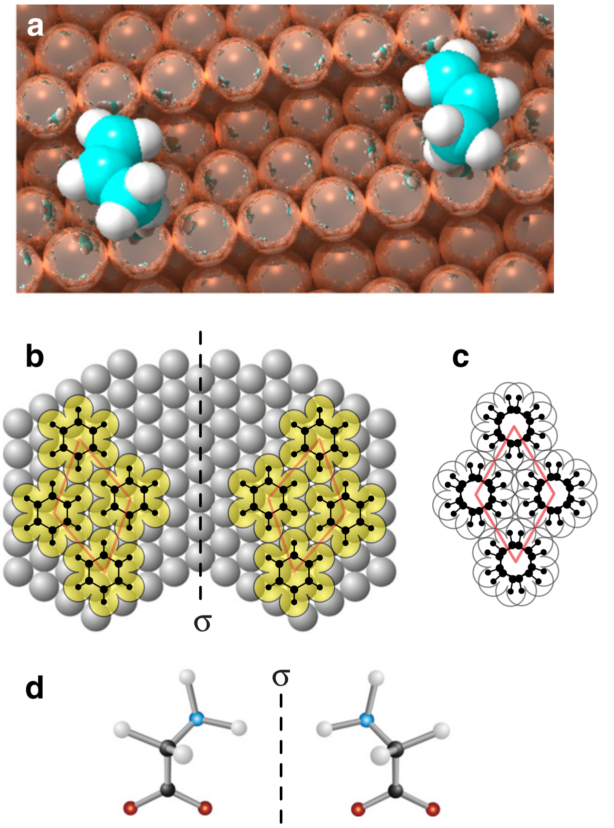

Fig. 2. Modes of mirror-symmetry breaking on a surface. a) Depending on which side is turned towards the surface, propene will form two adsorbate enantiomers. b) A single benzene molecule does not break the mirror symmetry of the substrate, but the alignment into a (3 1, −1 2) adlattice does. c) Superposition of both mirror domain unit cells shows that the benzene molecules do not become congruent. d) Chiral rearrangement of the molecular frame of glycinate, as viewed towards the surface.

2. Adsorption-induced chirality

On a surface only symmetry elements perpendicular to the surface plane are possible. Such lower dimensionality causes often mirror symmetry breaking upon adsorption. Sometimes, however, a polar or azimuthal tilt of the molecule or the rearrangement of the molecular backbone is responsible for creating a chiral adsorbate. There are many examples of molecules that become chiral upon adsorption. For example, pyruvic acid (α-keto propionic acid, Fig. 1b) will form either a left or right handed adsorbate with either side of the main molecular plane turning towards the surface. Another simple example is propene on Cu(211) (Fig. 2a) [29]. The two resulting static adsorbate configurations are enantiomers, because rotation and translation within the plane does not allow superposition of both configurations. Only rolling or flipping of the adsorbed species will cause inversion of enantiomers [29,30].

Beyond symmetry breaking at the single-molecular level, chirality may originate from a supramolecular arrangement of achiral adsorbates. In two dimensions, there are 17 plane groups [31], but only five of them (p1, p2, p3, p4 and p6) support chirality. Statistics performed on publications dealing with physisorption at the solid/liquid interface show that 80% of achiral molecules pack into chiral plane groups [32]. In particular the combination of close-packing of molecules and specific binding sites on a single crystal surface leads to chiral adsorbate lattices. An early example is benzene adsorbed on Ni(111) (Fig. 2c). The single molecule is aligned such that it does not break the mirror symmetry of the (111) surface. At monolayer saturation coverage however, a $\left(\sqrt{7}\times\sqrt{7}\right)$R19.1° structure is formed (better specified as (3 1, −1 2)[1] in matrix notation [33,34]). The adsorbate lattice now breaks the mirror symmetry and consequently, mirror domains are observed. The adlattice belongs to the p2 plane group and rotation by 180° superimposes both unit cells. However, considering the position of the molecules within the unit cell reveals that mirror-symmetry is absent (Fig. 2c). As for the hydrogen atoms in the benzene example, it is often interdigitation of molecular parts that lead to chirality at the level of self-assembly. In particular interdigitated alkyl chains are very common and lead to mirror symmetry breaking at the supramolecular level.

Finally, the molecular frame can be arranged into a chiral fashion due to specific interaction with the surface. A typical example is the achiral amino acid glycine (Fig. 2d). When bound to the surface as glycinate, the amino group can be oriented to the left or to the right with respect to the carboxylate group, inducing a chiral footprint on the surface.

3. Adsorption of intrinsically chiral molecules at surfaces

Somorjai and coworkers studied the adsorption of *(S)*-alanine on Cu(111) with LEED and reported an enantiomorphous (8 2, −2 6) structure [14] (denominated as $\left(2\sqrt{13}\times 2\sqrt{13}\right)$R13.6° in the original paper). This structure breaks the mirror symmetry of the underlying substrate, but mirror image-related patterns were not observed. Hence, the handedness of the single enantiomer was transferred into the entire layer. The same paper reports opposite mirror domains for *(R)*- and *(S)*-tryptophan, respectively. This early work therefore reports two important aspects of surface chirality: 1) the adsorbate lattice of chiral molecules is usually aligned in an oblique tilt with respect to the substrate lattice. 2) Other than for adsorption-induced chirality,

---

[1] We write here the (2 × 2) transformation matrix that links the adsorbate lattice vectors (b_1, b_2) to the substrate lattice vectors (a_1, a_2) *via* $b_1 = m^{11}a_1 + m^{12}a_2$ and $b_2 = m^{21}a_1 + m^{22}a_2$, in the form ($m^{11}$ m^{12}, m^{21} m^{22}).