Adsorption selectivity: a way to homochirality? Computational experiments

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Abstract

Life, as we know it today, is inseparable from homochirality; standing within the panspermia hypothesis, we investigate computationally the still unknown origin of the enantiomeric excess present in the organic matter of well-defined families of meteorites [1,2,3] through the possibilities open by a selective adsorption of the enantiomers.

1. Introduction

Two enantiomers have identical internal energies. When adsorbed on a same chiral surface, the complexes obtained are no longer enantiomers, but diastereoisomers. These diastereoisomers do not have the same energy. Assuming that we have a chiral interstellar surface at hand, we can consider the possibility to adsorb selectively one of the two enantiomers and thus engage a process of enantiomeric enhancement.

2. Selective adsorption

2.1 Modeling: Periodic model of the α-quartz surface { 1010 }

Quantitative results for adsorption energies are hard to get, experimentally as well as theoretically [4], taking into account that both, the nature of the surface and the nature of the molecule intervene in their own way. To address this problem, we rely on numerical simulations based on the methods of quantum chemistry, namely Density Functional Theory (DFT) that proved efficient in the periodic approach to this category of phenomena.

The periodic code used is VASP [5].

The active surface of infinite dimension is directly obtained by an appropriate cut of the crystal structure, and fully hydroxylated. to account for the nature of the interstellar grains. The dimensions of the unit cell, namely the horizontal interacting surface and the thickness of the slab, as well as the vertical separation between two successive slabs (vacuum), are determined in order to avoid spurious interactions between adsorbates due to the periodic treatment.

2.2 Example: Adsorption of lactic acid enantiomers on active surface of silica

Exploratory studies of the adsorption of simple molecules have shown different adsorption energies for different adsorption points on the same surface. In our case, aiming at rather small differences, we consider that the complexity of the α-quartz surface could potentially generate different adsorption sites with a different selectivity for chiral molecules.

In such conditions, a local adsorption is not representative and may lead to erroneous conclusions. We propose that *the selectivity of the surface is considered as a global property* and should be determined by a *statistical approach* illustrated on the case of lactic acid.

The following steps of such an approach are:

Extensive search on the surface for all adsorption sites optimized using the semi-empirical DFTB+ method (Tight Binding approximation) [6].

Determination of the different representative adsorption sites by means of geometric criteria and affectation of statistical weights to each of them.

Full treatment of each representative in the periodic "first principle model" to get reliable adsorption energies.

Calculation of the average adsorption energy characteristic of the couple adsorbate/surface as the sum of the adsorption energies of the most significant sites weighted by their occurrence numbers normalized to 100%.

For lactic acid, the results are illustrated in Figure 1 and the final difference so-obtained between the R and S enantiomers is [7]:

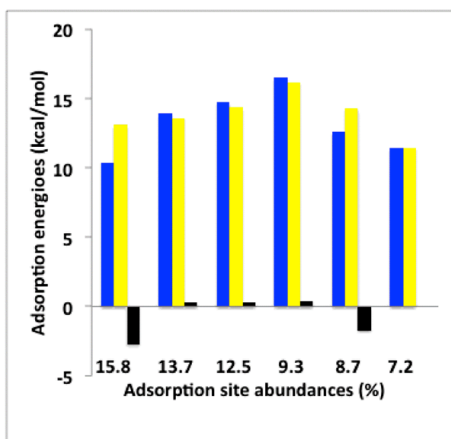$$\Delta E_{abs} = 0.7 \ kcal/mol = 0.03 \ eV.$$

Figure 1: Statistical budget for lactic acid adsorption. Colour code: Blue:R-enantiomer; Yellow:S-enantiomer; Black: R *vs* S adsorption selectivity.

3. Conclusions

For a given chiral molecule*, the adsorption is specific of the enantiomer* though the energy differences are found small, mostly *around 1Kcal/mole* (which corresponds to 0.04 eV or 500K).

The adsorption depends strongly of the site for complex surfaces and complex molecules. The question of the suitability of a statistic treatment could arise according the degree of complexity, the coverage of the surface and the precision needed.

For a *low* coverage, the energetically most favored position could be the only one to consider if the radiation flux to which the surface is submitted, is sufficient to induce non-destructive photo-desorption allowing re-adsorption on opportune positions.

For a coverage *close to a monolayer,* all sites will most probably be occupied and a statistical behavior should be observed.

If the complexity of the molecule allows a *reorganization of the topology of the adsorption site*, the larger will be the differences between sites and the more a statistics treatment will be necessary to get the global behavior of the surface.

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