

Desorption of Benzene, Pyridine, and Aniline from Calcite (10.4)

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Abstract

Nanostructures of π -conjugated molecules on insulator surfaces are of interest due to the ever-increasing demand for electronic devices on scales unachievable by conventional top-down approaches. Construction of such structures requires high precision and thus a thorough understanding of interactions between molecules and surfaces. Here we examined the desorption properties of benzene, pyridine, and aniline on the calcite (10.4) surface using temperature programmed desorption (TPD). These molecules were chosen in order to study the surface interaction with conjugated π -systems – that play a crucial role in two dimensional conductors – and the effect of heteroatoms on the anchoring of molecules.

Background

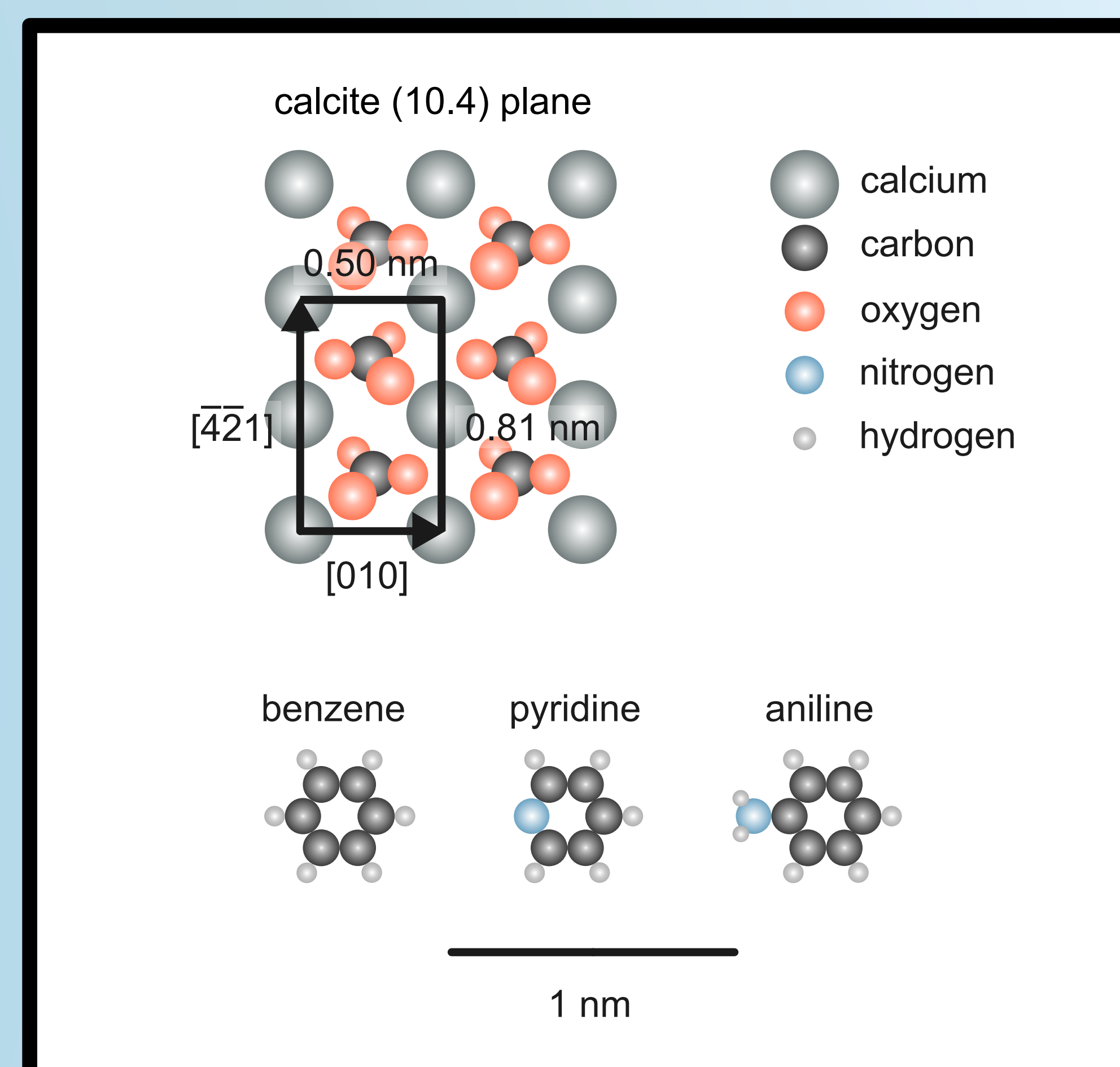
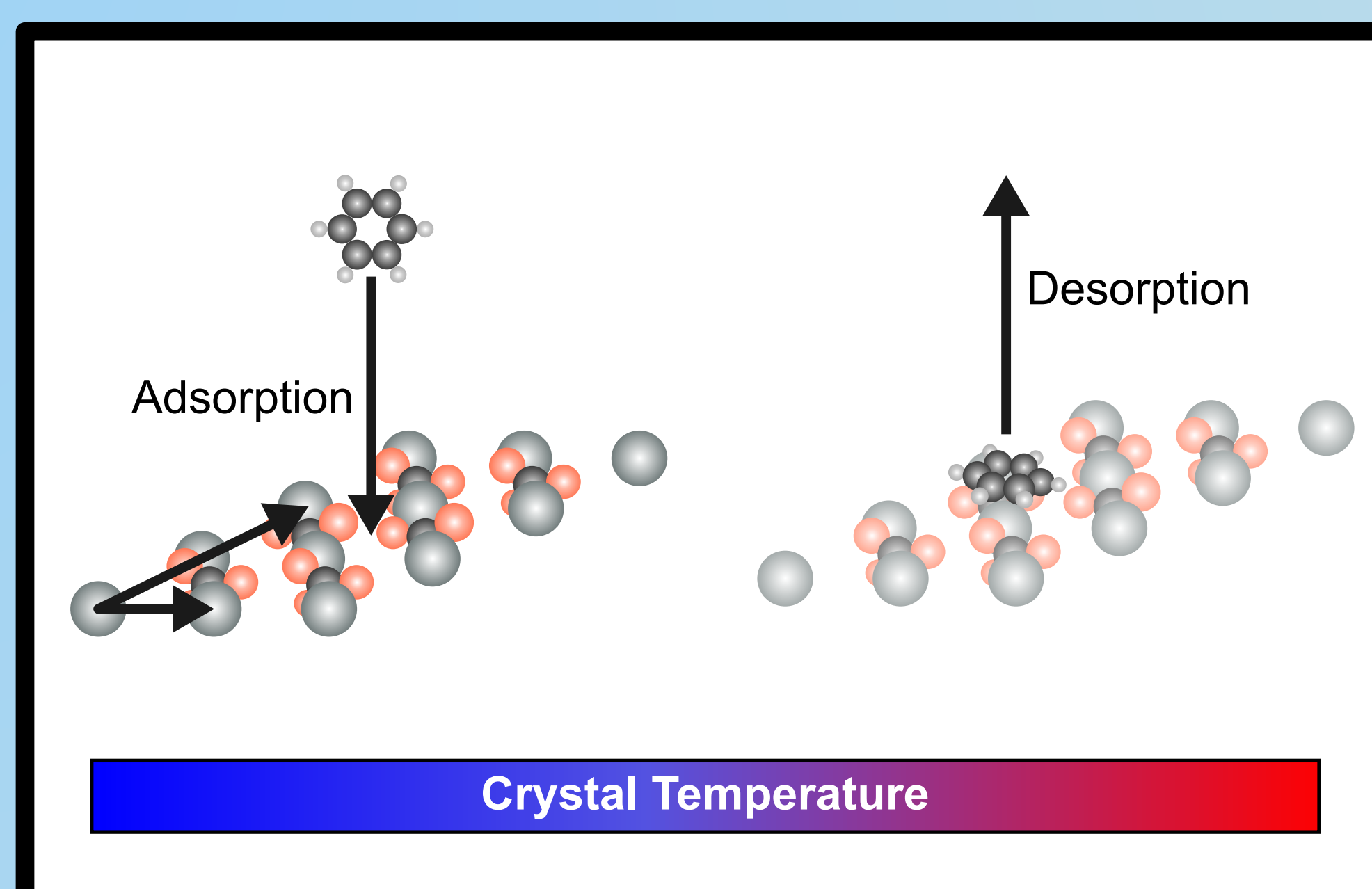
In this study the binding properties of three organic molecules on the calcite (10.4) cleavage plane were examined (fig. far right). The molecules were chosen to systematically study the anchoring effect of nitrogen containing functional groups.

Calcite is a naturally occurring mineral composed of calcium carbonate. Positively charged calcium cations and negatively charged carbonate anions form an insulating ionic crystal. A clean (10.4) surface is obtained easily from a single crystal by cleaving the crystal with a scalpel.

Benzene (C_6H_6) is an organic molecule composed of six CH-groups arranged in a planar "ring" shape. It is the model "aromatic" molecule, meaning it exhibits a so-called "conjugated π -system". In such π -systems electrons are delocalised which allows charge to move freely across the molecule. In large molecules, such as polymers, this can lead to unique electronic properties.

Pyridine (C_5H_5N) is similar to benzene, except that one CH-group is substituted by a nitrogen atom. Due to this, the electron distribution within the molecule is skewed slightly towards nitrogen, owing to its electronegativity. Therefore, stronger interaction with the ionic calcite surface is expected, compared to benzene.

Aniline (C_6H_7N) is benzene with one hydrogen atom substituted for an amine (NH_2) group. The introduction of an amine group breaks the symmetry and introduces a dipole moment. Additionally, the amine group may act as a hydrogen bond donor.



Method

We used temperature programmed desorption (TPD) to investigate the thermodynamic properties of the molecule-surface adsorption states. In TPD experiments a substance is first adsorbed onto a clean, cooled surface under ultra-high vacuum (UHV) conditions. The surface is then slowly heated while the rate of desorption – the number of desorbing molecules per second – is tracked (fig. above). This process is repeated a few dozen times for each molecule with varying surface coverages. The resulting rate-temperature curves (fig. below) are analysed to learn the desorption order, the adsorption energy ΔH and the change in entropy upon desorption ΔS .

Results

The adsorption energies ΔH are firmly within expectations. Benzene is the least polar molecule and exhibits the lowest value of ΔH (0.55 eV). The slightly stronger interaction (0.67 eV) observed for pyridine is owed to the aforementioned polarisation. Aniline exhibits the strongest interaction (1.0 eV) suggesting significant hydrogen binding. Theoretical calculations have provided further evidence for this assessment.

The rate curves (fig. left) show benzene, pyridine, and aniline reaching a maximum in their desorption rate at 186 K, 307 K, and 335 K, respectively. At first glance the stark difference between benzene and pyridine/aniline is unsurprising, for reasons mentioned. Interestingly however, the adsorption energy ΔH does not line up with these temperatures: ΔH of pyridine is much closer to the value of benzene than to ΔH of aniline.

A possible explanation is found within the entropy data. We found that pyridine is the only molecule to exhibit a decrease in entropy upon desorption (fig. below). The decrease in entropy is unfavourable and may explain the observed discrepancy between ΔH and the rate maxima. The negative ΔS value may arise from a conformational restriction as the molecule moves away from the surface; further study is necessary to determine the cause.

